NATIONAL
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PROGRAM

RADIOANALYTICAL METHODS MANUAL

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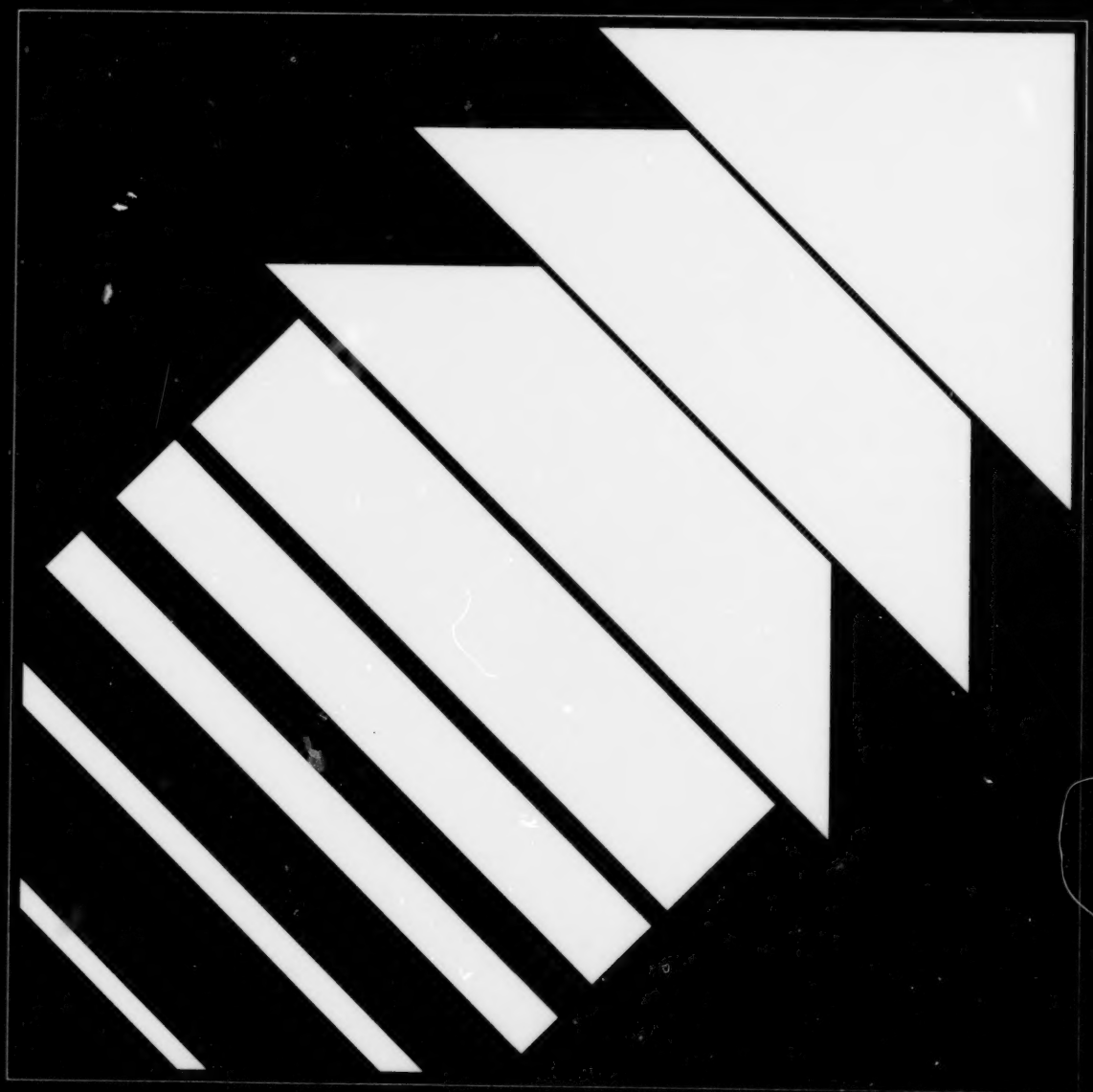

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RADIOANALYTICAL METHODS MANUAL

Monenco Consultants Limited: Norman W. Chiu and John R. Dean

National Uranium Tailings Program

NUTP-3E

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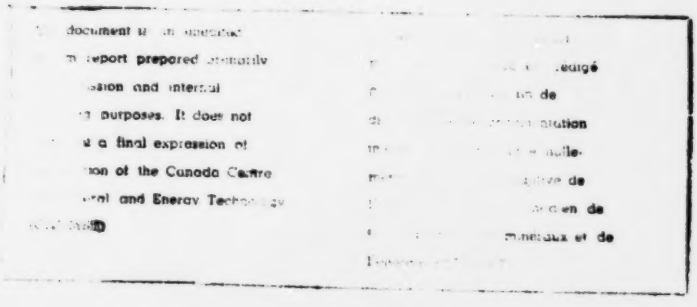

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FOREWORD

In Canada there are currently about 130 million tonnes of mine wastes (tailings) produced from the mining and milling of uranium ore that are on or near the surface. At public hearings and other forums held in connection with proposals for new uranium production facilities, concern has been expressed about the impact that these wastes may have on the environment in the future. Government regulatory agencies believe that there may be long-term environmental and health consequences associated with uranium tailings that are not yet fully understood.

As a result of a year-long study by a group of experts from government, industry and the universities, into the possible long-term problems of uranium tailings management, the Federal Government decided to launch an R & D program to assist in clarifying the nature and extent of problems that may arise in the future. It is anticipated that the results of such a program will be of use to the Atomic Energy Control Board and to provincial regulatory agencies in the establishment of criteria for the decommissioning and abandonment of uranium tailings. To this end, the National Uranium Tailings Program of CANMET has been funded to the extent of $9.5 million for a period of five years.

The main objective of this Program is to provide a scientifically credible information base that will assist government regulatory agencies in making confident, knowledgeable decisions, and in establishing criteria for the long-term protection of the environment and human health. The scientific information base will, among other things, describe the chemical and physical processes that involve tailings constituents and their movement along pathways from the tailings into the biosphere.

The National Uranium Tailings Program's activities, which have been entirely contracted out, have included research into the processes involved in the behaviour and movement of contaminants from tailings, field sampling and measurements, chemical analyses and predictive modelling. As an important part of the Program output, manuals have been prepared that incorporate the results of this work.

This manual has been prepared for the purpose of making available up-to-date information and data that will be of interest and practical use to those directly concerned with operational aspects of uranium tailings management and regulation.

W.G. Jeffery
Director General
Canada Centre for Mineral and Energy
Technology

AVANT-PROPOS

Environ cent trente millions de tonnes de déchets de mine (résidus) résultant de l'extraction et du broyage du minerai d'uranium reposent présentement en surface ou près de la surface du sol au Canada. Au cours des audiences publiques et autres débats tenus en vue d'étudier les propositions relatives à l'établissement de nouvelles installations pour l'exploitation de l'uranium, on a manifesté de l'inquiétude au sujet des répercussions environnementales futures des déchets de mines. Les organismes régulateurs du gouvernement croient que les résidus d'uranium peuvent, à long terme, avoir des conséquences dont la gravité nous échappe actuellement, sur l'environnement et la santé des travailleurs.

Pour donner suite à une étude d'une durée d'un an à laquelle a participé un groupe de scientifiques du gouvernement, de l'industrie et des universités et qui portait sur les problèmes à long terme que pose la gestion des résidus d'uranium, le Gouvernement fédéral a élaboré un programme R-D en vue d'élucider la nature et l'étendue des difficultés qui pourront se poser à l'avenir. On espère que les résultats de ce programme permettront à la Commission de l'Énergie atomique du Canada et aux organismes régulateurs provinciaux de procéder plus facilement à l'élaboration de normes relatives au processus d'abandon des résidus. À cette fin, le gouvernement à financé jusqu'à concurrence de 9,5 millions de dollars le Programme de gestion des résidus d'uranium du CANMET, et ce, pour une période de cinq ans.

Le but principal du Programme est de fournir une source d'information scientifique valable qui permettra aux organismes régulateurs du gouvernement de prendre des décisions avec assurance et en toute connaissance de cause et d'établir des normes de protection à long terme de la santé des travailleurs et de l'environnement. La banque d'information scientifique fournira la description, entre autre, des processus physiques et chimiques auxquels participent les éléments constituants des résidus de mine et du cheminement de ceux-ci dans la biosphère.

Les activités du Programme national de recherche des résidus d'uranium, qui ont toutes été adjugées par contrat, comprennaient des travaux de recherche sur les processus relatifs au comportement et au mouvement des impuretés provenant des résidus, des échantillonnages et des mesures sur le terrain, ainsi que des analyses chimiques et la modélisation prophétique. Les résultats de ces activités sont présentés dans des guides dont la publication fait partie intégrante du Programme.

Ce guide a été préparé afin de fournir à toutes les personnes qui s'intéressent activement aux aspects opérationnels de la gestion et de la régulation des résidus d'uranium, des données récentes et des renseignements intéressants et utiles.

W.G. Jeffery
Directeur général
Centre canadien de la technologie des minéraux

PREFACE

The preparation of this laboratory manual was carried out under the terms of DSS Contract Serial Number 0SQ83-00134. It is intended as a reference guide to assist participants in the National Uranium Tailings Program (NUTP) to meet its analytical requirements.

The terms of this contract were that it should (within certain limitations) be a compendium of the best available methods for each parameter. Recommendations were to be made, by the contractor, of the method(s) most appropriate to the NUTP.

Norman W. Chiu and John R. Dean
Monenco Consultants Limited
March 1984

DISCLAIMER

This manual was prepared for the National Uranium Tailings Program, CANMET, Energy, Mines and Resources Canada. References herein to any specific commercial product, process or service by tradename, trademark, manufacturer or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favouring for use. The views and opinions expressed herein are those of the authors only.

The methods detailed in this manual have been found to produce the quoted precision and accuracy by experienced chemical laboratory staff with the specified analytical instrumentation on the type of materials that are customarily analysed. The Canadian government neither makes any warranty, express or implied, nor assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or method disclosed.

ABSTRACT

This *Radioanalytical Methods Manual* is comprised of 12 chapters. It includes a review of the pertinent literature up to the end of 1982 pertaining to the measurement of the radioactive species listed under the terms of the contract. Included is methodology recommended for the decomposition of soils, tailings, ores, biological samples and air filters. Detailed analytical methodology for the measurement of gross alpha, gross beta, gross gamma, uranium, radium-226, radium-228, lead-210, thorium-232, thorium-230, thorium-228, total thorium, radon-222, radon-220 and radon-219 is presented.

INTRODUCTION

In January 1979, CANMET published a report entitled *Radiochemical Procedures for the Determination of Selective Members of the Uranium and Thorium Series* (CANMET Report 78-22 G.L. Smithson, J.L. Dalton and D.L. Masson). Many of the methods given and equipment discussed in this report were at their early stages of development. In the intervening years a great deal of work has been done by many workers to improve these radioanalytical techniques. The National Uranium Tailings Program (NUTP) recognized that it should sponsor a new radioanalytical methods manual. A contract was therefore placed with Monenco Consultants Limited of Calgary.

I would like to thank Dr. Norman W. Chiu and Dr. John R. Dean of Monenco for their efforts in assembling this manual. Their intimate knowledge of the current state-of-the-art and its practical application in a working laboratory is clearly reflected in this work. In addition, I wish to thank Dr. Clint W. Smith for his review of the statistical portions of each method and for the preparation of the Appendix A on the estimation and reporting of procedural uncertainties in radiochemical determinations. I also wish to thank Mr. Lloyd Dalton and Dr. Gene Smithson for the very thorough editing they did. Their efforts ensured that this document met the scientific and editorial standards required by CANMET.

A number of other people also contributed to this project at various times. The efforts of all of these people have been greatly appreciated by the NUTP staff. The result is a manual which will serve radioanalytical chemists for many years to come.

Roy John
Project Manager, Measurements
National Uranium Tailings Program

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1. REVIEW OF RADIOCHEMICAL METHODOLOGY

This chapter contains a review of the recent literature pertaining to the radiochemical measurement of certain, naturally occurring, radioactive elements. Non-radiochemical methods for the determination of uranium are also reviewed. To assist the reader, a summary of the uranium-238, uranium-235 and thorium-232 decay series is shown in Figure 1.

1.1 RADIUM-226

Radium-226 is the most frequently determined radionuclide because it can be used as a measure of radioactive contamination of the environment. It can be determined by five methods; namely, gross alpha measurement, radon emanation, alpha spectroscopy, gamma ray spectroscopy and coincidence spectroscopy.

Gross alpha counting (1–3) is the simplest and most economical method. It involves the removal of radium as sulfate from the sample solution with lead sulfate carrier. Radium sulfate is then isolated by dissolving the radium-lead sulfate in alkaline EDTA or DTPA and coprecipitating with barium sulfate carrier at pH 4.8. The radium-barium sulfate is counted on a gross alpha counter. This gives total radium. To obtain radium-226, one must correct for the presence of radium-223 and radium-224 by differential decay analysis.

Radon emanation (3–14) is an indirect method based on the relationship between the activity of the radon-222 daughter measured to that of the radium-226 parent present. Radium is removed from the sample solution and purified as for the gross alpha counting. The radium-barium sulfate is redissolved in alkaline EDTA and placed in a bubbler, from which the gaseous radon is stripped after a suitable ingrowth period has elapsed. The gas is transferred to a ZnS scintillation (Lucas) cell and counted on a scintillation counter. With this method, there may be a considerable delay between sealing the bubbler and stripping the gaseous radon from the solution. For example, if 50% equilibrium

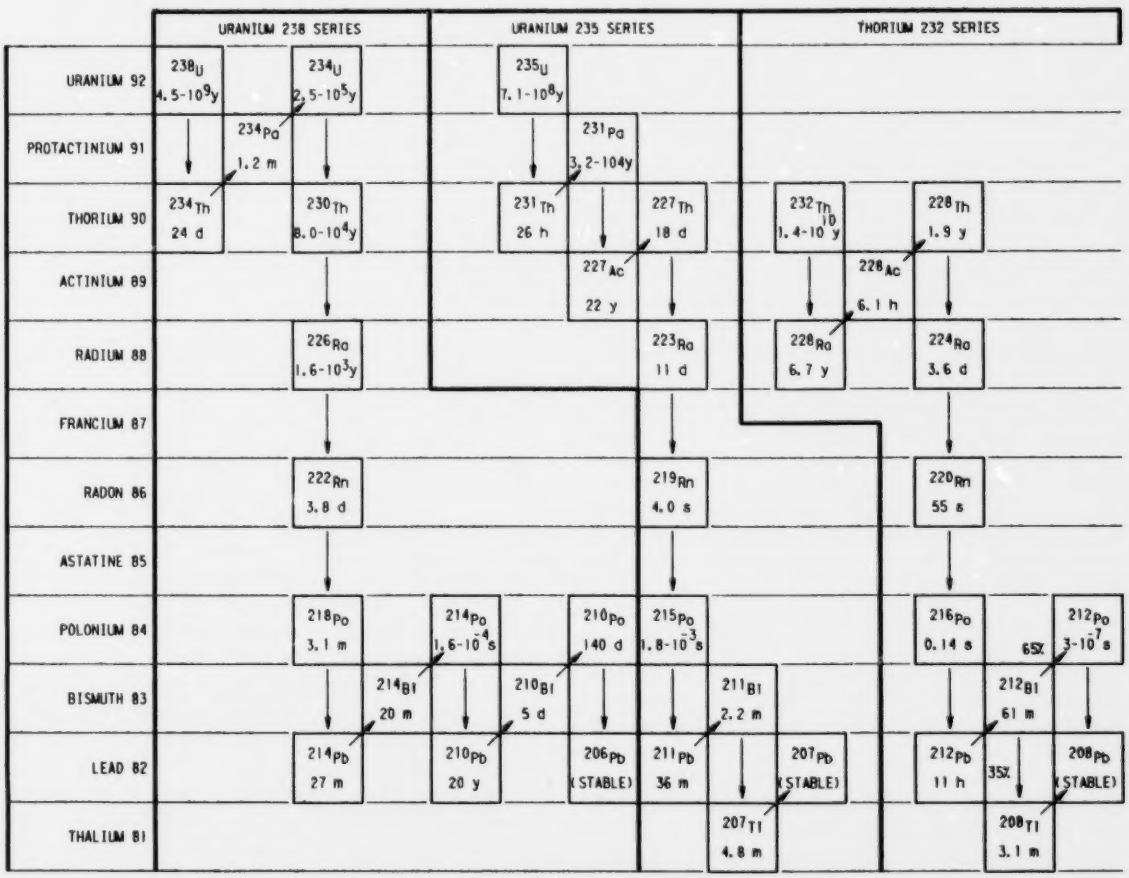

Fig. 1 – Some important characteristics of the U-238, U-235 and Th-232 series decay chains.

between radium-226 and radon-222 is desired, a waiting period of one half-life is necessary, i.e., about four days. In practice, however, ingrowth periods vary a great deal depending on the end-use of the analytical result and the quantity of radium-226 present in the sample.

In the emanation procedure, there are numerous modifications of the radon-222 measurement and the radium-226 preconcentration. Modifications in the measurement include the use of a simplified scintillation cell (15), an ionization chamber (16) or liquid scintillators (17). Modifications in the preconcentration of radium include coprecipitation with calcium carbonate in the presence of activated carbon (18) or with calcium phosphomolybdate in the presence of polyethylene glycol (19,20) or by adsorption on a cation exchanger (10) or fibre impregnated with manganese dioxide (21–24). The preconcentration step can even be omitted by storing the sample in a 20-L glass bottle and extracting radon directly (25–27). Some workers concentrate the radon emanating from large volumes of water into a liquid nitrogen trap and later release it by warming (11,14,16).

High-resolution gamma spectroscopy requires the use of Ge(Li) or high-purity N-type Ge detectors (21,28,29). This technique is based on the simultaneous determination of radionuclides by measurement of emitted gamma photons from 40–2000 KeV. In certain instances, it can be complicated and time-consuming because of the presence of large numbers of gamma photopeaks but simplification is possible if the radionuclide(s) of interest is (are) physically separated from the others. For example, Michel et al. (21) successfully determined the activities of radium-226 and radium-228 by separating radium with barium carrier from the sample. For the determination of radium-226, photopeaks of its daughters lead-214 (295 KeV, 352 KeV) and bismuth-214 (609 KeV, 1120 KeV) were used. If uranium-235 is absent from the sample, the 185 KeV line from radium-226 can be used. Similarly for radium-228, the photopeaks of its daughter actinium-228 at 338 KeV, 911 KeV and 965 KeV were used. Other investigators have reported the use of gamma spectroscopy to determine uranium (30), thorium (30) and lead-210 (31).

Coincidence spectroscopy has recently been reported for the determination of radium-224, radium-226 and radium-228 (32,33). The coincidence spectrometer consists of a NaI(Tl) gamma detector and an alpha-beta detector which are connected to a coincidence analyzer and associated electronics. The technique is based on the separate measurement of the coincident alpha-gamma transitions of radium-226 and radium-224, and the coincident beta-gamma transitions of actinium-228, the daughter of radium-228 (34). Chemical separation and purification of radium into a source is necessary. Radium-224 and radium-226 are measured directly and radium-228 is measured indirectly via its daughter actinium-228. This eliminates the requirement of separating actinium-228 from radium-228 which restricts the detection sensitivity because of the short half-life of actinium-228 (6.13 h).

Alpha spectroscopy involves the direct measurement of the alpha emission from radium-226. The high resolution and low background of surface barrier detectors provide specificity and high sensitivity. Source preparation usually involves coprecipitation of radium sulfate with barium sulfate (35–39). The spectral resolution obtained depends on the quantity of barium carrier, the size of the barium sulfate crystals and the presence of other insoluble impurities. However, when the quantity of barium carrier is reduced to improve the resolution, the chemical yield decreases. Lim and Davé (38) have reported alpha resolutions of 229 KeV to 496 KeV (FWHM) for 100 μg to 1 mg of barium carrier, coupled with chemical yields of 65–85%. Dean and Chiu (40) have reported alpha resolutions of 120, 156 and 221 KeV for 68, 138 and 276 μg of barium carrier, respectively. Sill (41) has indicated recently that with complete sample dissolution, a modification of the barium sulphate precipitation procedure, and removal of insoluble impurities from all reagent solutions, one can obtain both high alpha resolution (60 KeV) and high chemical yield. Electron microscopy has shown that barium sulfate crystals obtained by the normal precipitation from hot DTPA solution are angular and relatively large, at least 1 μ on a side (41). They tend to form large clusters on the membrane filter so that the fraction of the total available filter area actually covered is small. Consequently, the effective thickness of the deposit is much larger than for a uniform distribution of smaller crystals. On the other hand, barium sulfate crystals obtained by precipitation from DTPA solution at room temperature, using a barium sulfate seeding suspension, are almost amorphous (<1 μ) and they cover the entire surface area of the filter. The alpha resolution is found to be 68 KeV for 100 μg of barium carrier, which compares favourably to 50 KeV by electro-deposition on a polished stainless steel disc (35). Even with 500 μg of barium carrier, the alpha resolution is an acceptable 155 KeV.

1.2 RADIUM-228

Because of the difficulty in measuring the very low-energy beta emission of radium-228 (0.055 MeV), all techniques reported to date are based on the indirect measurement of its daughters, actinium-228 (6.1 h half-life), thorium-228 (1.9 y half-life) or lead-212 (10.6 h half-life). The application of gamma spectroscopy and beta-gamma coincidence spectroscopy for the measurement of actinium-228 has been discussed earlier. The most widely used tech-

nique is beta counting of actinium-228 (1–3,4–6,8, 22,23,42–55) which requires less than two days for equilibration between radium-228 and actinium-228. A few procedures use alpha spectroscopy to measure the long-lived daughter thorium-228 (5,56) or beta counting of the short-lived daughter lead-212 (57,58). Both of these procedures require 6–12 mo for the ingrowth of daughters, which is unacceptable for routine measurement.

Radium-228 must be separated from other radionuclides before its daughter, actinium-228, is allowed to grow in. After ingrowth, actinium-228 is removed and beta counted immediately because of its short half-life of 6.1 h. In general, radium-228 together with all other radium isotopes are separated and purified by coprecipitation with barium sulfate, as discussed earlier. Actinium-228 can be separated from its parent by solvent extraction or by ion exchange and then can be either electroplated on a polished metal disc, evaporated on a stainless steel planchet, or coprecipitated with a carrier for beta counting. A faster and more efficient procedure is used by Chiu and Dean (59). Radium is separated and purified in the form of barium-radium sulfate. After the ingrowth of actinium-228, the sulfate is dissolved in alkaline EDTA or DTPA and the actinium-228 is precipitated as the hydroxide with cerous hydroxide as the carrier (60) and collected on a membrane filter for immediate beta counting. The entire procedure takes less than 30 min, which permits the preparation of one sample to be completed just as the beta counting of another is finished, thereby reducing the risk of decreased sensitivity while an actinium-228 source is waiting to be counted.

1.3 LEAD-210

The radioactivity of lead-210 is normally measured indirectly by alpha counting of its daughter polonium-210 (5.3 MeV, 138 d half-life) or by beta counting of its daughter bismuth-210 (1.17 MeV, 5 d half-life) because of the low-energy beta emission of lead-210 (0.018 MeV). The appropriate methodology depends on the state of equilibrium between lead-210, polonium-210 and bismuth-210.

If radioactive equilibrium is known to exist, the measurement of polonium-210 by alpha spectroscopy is preferred. Polonium-210 in an aqueous solution can be extracted by spontaneous deposition as the free element on a disc of a less noble metal, such as copper (61,62), nickel (63–68) or silver (63,67,69–71). Nickel and silver are better than copper for the extraction of polonium-210, although nickel also extracts bismuth-210 and some lead-210 (up to 20%). However, since polonium-210 is an alpha emitter and bismuth-210 and lead-210 are beta emitters, this method is specific for the indirect determination of lead-210. It is very sensitive because of the high-resolution alpha source obtained. The chemical procedure is relatively short and the plating can be done in two hours at 60–65°C. Polonium-208, also an alpha emitter, is recommended as a tracer.

If the degree of radioactive equilibrium is unknown, then three techniques are available. The first is to measure polonium-210 in a sample three to six months after the removal of the initial polonium-210 by spontaneous deposition on a nickel disc (63). The second is to measure the bismuth-210 ingrowth five or more days after separating lead-210 from the sample (3,72–75). The third is to allow the sample to age for 30 days, during which time complete equilibrium between lead-210 and bismuth-210 will be ensured to greater than 98%. The bismuth-210 is separated from lead-210 and determined by measurement of its beta activity.

Lead-210 can be separated by several techniques such as electroplating (76,77), solvent extraction (74,78–81), ion exchange (82–85), chromatography (86–88) and electrochromatography (89,90). All these techniques are labour-intensive and very time-consuming. The simplest procedure involves a single extraction of bismuth-210 with a 0.1% solution of DDTC in chloroform (91) from a 2N hydrochloric acid solution. Bismuth-210 is subsequently precipitated as bismuth oxychloride and collected on a membrane filter for beta counting. A modification to the apparatus allows extraction in batches of six or twelve under identical conditions and eliminates the use of separatory funnels (59). An isotopic, gamma-emitting tracer, bismuth-207, is used for the chemical recovery measurement.

A recent report by Schery (31) indicates that the direct measurement of a 47 KeV photon emitted by lead-210 has not been successful in the past because of the self absorption in the sample and the low sensitivity of standard Ge(Li) detectors to this low-energy photon. However, a new generation of high-purity N-type germanium detectors (92) now available are characterized by improved sensitivity to low-energy photons and increased active surface area. Therefore, direct assay of lead-210 in moderately sized environmental samples may be possible by measuring the 47 KeV photon.

1.4 THORIUM ISOTOPES

The long-lived thorium isotopes from the uranium and thorium series, thorium-230 (8×10^4 y half-life) from the uranium-238 series, thorium-232 (1.4×10^{10} y half-life), and its daughter, thorium-228 (1.91 y half-life), emit alpha particles with energies of 4.6 MeV, 4.0 MeV and 5.3 MeV, respectively. They can be determined simultaneously after separation from all other radionuclides and deposition as a very uniform and thin source for best alpha spectrometric resolution.

The purification of thorium by solvent extraction has been found effective using bis(2-ethylhexyl)phosphoric acid (6,73), Aliquat-336 (93,94) thenoyltrifluoroacetone (3,95), trilaurylamine (96), Alamine-336 and Primene JM-T (97) in combination with ion exchange has also been used (98). Electrodeposition on a polished stainless steel disc has been found to be the best method of preparing a uniform thin source for alpha spectroscopy for best resolution. However, this technique is time-consuming and requires elaborate electrodeposition apparatus and Sill and Williams (60) have developed an alternate method. The purified thorium isotopes are precipitated as hydroxides with 50 μg of cerium carrier from a strongly alkaline solution of EDTA or DTPA and is collected on a 0.1-μ membrane filter for high-resolution alpha spectroscopy. The alpha resolution is about 65 KeV FWHM and compares favourably to the 50 KeV FWHM for electrodeposition (35). For chemical recovery, thorium-234 tracer (99) is commonly used.

Another method uses a combination of high-resolution gamma spectroscopy and alpha spectroscopy (98). Thorium-228 is measured on the original sample by gamma spectroscopy and the isotopic ratios of thorium-228, thorium-230 and thorium-232 are determined by alpha spectroscopy on the thorium source after extraction. By means of the thorium-228 activity and the isotopic ratios so obtained, the activities of thorium-230 and thorium-232 are calculated. A similar approach by Dean and Chiu (40) measures thorium-228 indirectly via its radium-224 daughter by alpha spectroscopy. After ensuring equilibrium between thorium-228 and radium-224 (20 d), radium-224 is coprecipitated with barium sulfate for alpha spectroscopy. The main advantage of this approach is that barium-133, a gamma emitter and a proven tracer for radium, is used.

1.5 RADON

Radon isotopes occur in all three naturally occurring radioactive decay series (Fig.1). Radon-222 (3.82 d half-life) occurs in the uranium-238 series, radon-219 (4.0 s half-life) in the uranium-235 series and radon-220 (55.3 s half-life) in the thorium-232 series. Radon is a gas and the distance each isotope can travel from its origin depends on its half-life. Radon-222 with a 3.82 d half-life can be transported many miles from its source. An average concentration in air of 0.002 Bq/L and it is generally considered that exposure to the inhaled, short-lived decay products of radon-222 constitutes the main natural irradiation of the human respiratory tract (100). In areas of Brazil and India the presence of surface deposits of monazite sand results in high levels of radon-220 in the surrounding atmosphere (101–103). As a result of these concerns, a large number of sampling and measurement techniques have been developed for radon isotopes and their daughters. They include counting of alpha disintegrations in Lucas chambers, gamma spectroscopy (after concentration on charcoal), pulse-type ionization counting chambers, Track Etch detection and thermal luminescence. The methods that can be used to sample the gases and aerosols, before measurement, can be categorized into three groups: 1) grab sampling, 2) time-integrated sampling, 3) continuous monitoring. The most appropriate technique depends largely on the application of the measured data.

1.5.1 Grab Sampling Methods

Grab sampling techniques use silver-activated zinc sulfide (ZnS) phosphor alpha detectors developed by Lucas (11), and are still among the most sensitive. Alpha particles emitted by the radon isotopes and their daughters impact the ZnS scintillation material, creating energy pulses in the form of light quanta which are detected and amplified by a photomultiplier tube. Each alpha particle striking the phosphor is counted and the counts are accumulated for a suitable period of time. This technique will not differentiate between an alpha particle emitted from radon-222 and its daughters and one emitted from, for example, radon-220. Lucas detectors with higher sensitivity, lower backgound and better reproducibility than the conventional model referred to above, have been developed and described (104–106). Large-volume electrical-gradient Lucas cells, which have sensitivities of the order of 0.0004 Bq/L, have been developed (107).

The acquisition of the grab sample can be made by use of a bulb-type hand pump which transfers the gas into the ZnS chamber. A typical analysis procedure is to count for three consecutive one-minute intervals to allow the ingrowth of radon-222 daughters and the decay of any radon-220 that may be present. A formula, using the three one-minute measurements, is then used to determine the radon content of each gas sample (108). An automated instrument that is micro-processor controlled is now available (109). It measures and subtracts the background, and obtains a gas sample using an internal time-controlled pump. After a 5- or 15-min analysis period, the instrument will calculate the radon isotope activities in the grab sample and will then automatically resample.

1.5.2 Time-Integrated Sampling

The emanation of radon from the surface of the earth, or from uranium mine tailings, is influenced by meteorological conditions, such as barometric pressure, wind speed, temperature and water content of the solids. Because various atmospheric fluctuations can alter instantaneous radon concentrations, the preferred method of sampling and measurement is to integrate over periods of several days or weeks. There is also an improvement in accuracy and precision over grab sampling by averaging the short-term fluctuations in the radon measurements.

The original device used for integrated radon-222 measurements is a Track Etch cup with an alpha particle–sensitive plastic strip in the enclosed end (110–112). This technique is based on the principle that alpha particles produce latent tracks in a cellulose-based film that can be observed microscopically after development with a caustic solution (113). Interferences from radon-220 can be lessened by covering the open end of the Track Etch cup with a permeable membrane that delays the migration of the radon isotopes into the cup, allowing time for the short-lived radon-220 (5.5 s half-life) to decay to insignificant levels. The condensation of water vapour on the detector strip can reduce the signal from radon but this can be eliminated by using a desiccant within the membrane-enclosed cup. The sensitivity of the technique is claimed to be 0.14 Bq/L (114). Track Etch cups are only available through the Terredex Corporation, California.

Maki and Tanaka (115) have described a modification of the alpha track method which they claim is six times more efficient than the conventional method. It involves collection of radon daughters on a light bulb. Other devices incorporating the use of a cellulose-based film are now commercially available.

Activated charcoal is a material widely used (114) for adsorbing and retaining radon on a time-integrated basis. It differs from Track Etch in that radon is trapped over a time interval and the time-averaged sample is analysed at the end of the collection period. The radon measurement can be made in several ways: indirectly, by counting the bismuth-214 gamma emitting daughter of radon-222 using a NaI crystal; by desorbing the radon from the charcoal using heat, followed by measurement in a ZnS phosphor detector; by removal of the radon from the charcoal by solvent extraction (116) followed by determination using a liquid scintillation counter (117).

Shearer and Sill (118) and Sill (119) described a method of collecting time-integrated atmospheric samples for radon in which a small aquarium aerator pump forces air through a precision needle valve into a 40-L laminated Mylar bag at 10 mL/min to give a volume of 30 L in each 48-h sampling period. A known volume of this atmospheric sample is passed through an activated charcoal filter at low temperature to adsorb the radon. The charcoal is then heated to remove the radon which is then transferred to an alpha-sensitive scintillation cell. Other measurement techniques discussed above, such as solvent extraction or gamma counting, could also be used depending on the concentration of radon collected.

Thermoluminescence is a property whereby certain substances store energy that is released in the form of light when the substance is heated. This principle is commonly used in radiation-monitoring dosimeters called thermoluminescent detectors (TLD). They are sensitive to alpha, beta and gamma radiation.

Time-integrated radon monitors based on the use of TLD's have also been developed. One type is based on the aspiration of air through a two-filter tube (0.45-μg pore size) at a known flowrate. Placing the TLD after the second filter permits determination of gaseous radon, whereas placing the TLD between the first and second filter permits the determination of the airborne, aerosol-type, radon progeny which are not able to pass through either filter. The detection limit was found to be 0.002 Bq/L for an integration period of one week. The second type of time-integrated TLD system involves permeation of radon through a porous barrier. The detection limit with this system has been reported (103) to be 0.01 Bq/L for an integration period of one week. The thermoluminescent method is a potentially powerful technique and may become a serious competitor of Track Etch.

Another type of integrating system is called a passive monitor and is used primarily indoors. It is based on the design of George and Breslin (120) and is manufactured by EDA Electronics Inc. of Toronto. The lower limit of detection (at the 95% confidence limit) is reported to be about 2 Bq/L·h or 0.01 Bq/L for a one-week sample period (121). The passive monitor has been found to give results comparable to the Track Etch method but its greater sensitivity allows shorter monitoring periods.

1.5.3 Continuous Monitoring

Many continuous monitors have been developed (122–125). A modification to the principle of introducing a discrete sample into a ZnS detector is the continuous sampling technique employed by the Eberline Instruments model R6M-1 system. The atmospheric sample is continuously drawn through the cell and flowmeter by a pump. The alpha particles from radon-222 decay and that of its progeny are recorded and related to the radon-222 content by calibration using a reference gas. This technique is subject to errors that can result from attachment of the non-gaseous radon progeny to the surface of the cell. Unless a period of time is allowed between measurements for these daughters to decay, the data are not strictly representative of radon contained in the sampled gas (103, 104).

Schery et al. (126) have described a two-filter continuous monitor method specific for radon-222. Air enters through the first filter which removes all activity except radon. As the air moves between the filters, radon undergoes decay and its daughter products are deposited on the second filter, on which they are counted by a detector. From the concentration of the daughters, it is possible to calculate the concentration of radon in the original air.

A sensitivity of 0.0004 Bq/L for radon-222 was reported. Field trials indicate high reliability and maintenance-free operation for periods of more than a week. Nazaroff (127) and Perdue et al. (128) have described continuous methods for measuring radon progeny based on alpha spectroscopy. Consideration is given to the applicability of elucidating activities of radon-219 and radon-220 from the information received. These methods are modifications to the two-filter technique described by Schery et al. (126).

Czarnecki et al. (109) compared the detection limit and sensitivity of the instantaneous ZnS phosphor analyzers of EDA Ltd. Canada (model EDA-RD-200) and Bendix Corp (model TSA RE-350) with those of Track Etch. The results are shown in Table 1.

1.5.4 Recommended Procedure for Atmospheric Radon Measurement

As described above, there are several techniques available for monitoring atmospheric levels of radon. A choice can be made among grab sampling, integrated sampling and continuous monitoring. They encompass a variety of experimental techniques with a wide range of sensitivities and properties.

For the purpose of this manual, time integration has been chosen as the most appropriate method. A continuous technique could have been chosen but inherent time delays often do not offer significant advantages over integrated methods. Since radon concentrations are known to fluctuate rapidly, grab sampling is not considered to be an optimal approach.

The integrated sampling method by Sill (119) has been chosen for its simplicity and the low cost of the equipment required. Samples are collected continuously for a period of several days. During this period the radon will be undergoing decay. The fraction remaining at the end of the sampling period can be approximated by using one-half of the sample time in calculating the decay factor, $e^{-\lambda t}$. The error in this simplification is less than 2.5% for sample times of up to 100 h.

1.6 URANIUM

The analytical chemistry of uranium was extensively investigated as part of the Manhattan Project (129). Since then, a number of measurement techniques have been developed. These include fluorometric, gravimetric, volumetric, spectrophotometric, coulometric, polarographic, alpha-particle counting, gamma spectrometric, neutron activation analysis, fission track analysis and x-ray fluorescence. Several review articles and manuals have been published (129–134).

Spectrophotometric and fluorometric methods are extensively used for the measurement of uranium. The most common spectrophotometric reagents are Arsenazo III (135–143), 4-(2-pyridylazo)resorcinol (144–147) and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (148–150). Lyle and Tamizi (149) have developed an automated spectrophotometric method using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol for which up to 60 samples per hour can be determined. The detection limit is 0.2 mg/L. The ultraviolet radiation excited fluorometric method (151–160) is both reliable and sensitive for the determination of uranium. The application of a laser-induced fluorometric method (161–169) can extend the detection limit to 5 pg of uranium (167,168). This method virtually eliminates interferences from quenching substances. It also eliminates the need for organic extraction and the subsequent fusion process since the determination is done in aqueous solution.

The determination of uranium by the neutron activation-delayed neutron counting technique (170–177) is very accurate and reproducible. The detection limit in solids is 0.1 μg of uranium. Brits and Smith (173) preconcentrated uranium in natural water by adsorbing the uranyl thiocyanate complex on an anion exchange resin and determining uranium on the resin directly by delayed neutron counting. The detection limit is 0.01 μg/L. Holzbecker and Ryan (174) determined uranium in water down to 30 ng/L by both thermal neutron and epithermal neutron activation. Preconcentration on activated carbon was used for samples containing less than 4 μg/L. Kuleff and Kostadinov (175) and Hirose and Ishii (176) reported the use of epithermal neutron activation coupled with high-resolution gamma spectroscopy for the determination of uranium.

Recent advances in the design of X-ray fluorescence spectrophotometers make possible the direct and rapid determination of low levels of uranium in solids. When combined with preconcentration techniques, nanogram amounts of uranium in water can also be determined. Both wavelength-dispersive (178,179) and energy-dispersive (180,181) X-ray fluorescence techniques have been used.

The application of atomic absorption spectroscopy for the determination of uranium is not practical (182,183) because of low sensitivity due to the high thermal stability of its oxide (184). However, an indirect method, reported by Alder and Das (185,186), shows promise. It involves the quantitative reduction of Cu^{II} to Cu^{I} by U^{IV}. The Cu^{I} ions are complexed with neocuproine, extracted into chloroform, back-extracted into hydrochloric acid solution and measured by either flame or graphite furnace atomic absorption spectroscopy. The sensitivity is 5 μg of uranium with the upper limit being 500 μg without dilution. Scott et al. (187) and Homi and Manabe (188) reported the determination of uranium in solution by ICP-atomic emission spectroscopy. The high temperature, >6000°K, of the inductively coupled argon plasma is sufficient to dissociate the uranium oxide species for measurement. The detection limit is 0.3 mg/L.

Table 1. Characteristics of radon detectors determined with the radon calibration unit*

Detector	Detection Limit (Bq/L)	Sensitivity (Bq/L Integral Count)	Coefficient of Variation ± %
EDA RD-200	0.44	0.078	11
TSA RE-350	0.48	0.082	13
Track Etch	0.06	0.01	16

These measurements were established by exposing the instruments to a known controlled radon environment.

*Taken from reference 109.

2. SAMPLE DECOMPOSITION FOR RADIOCHEMICAL ANALYSIS

2.1 PRINCIPLE

One of the most important steps in any radiochemical procedure is the complete decomposition of a sample matrix. Also the element sought must be converted reliably to the proper ionic form before chemical reactions, characteristic of that element, can proceed. The accuracy of radiochemical analysis depends on the choice of the sample decomposition method. The following are some of the commonly used methods:

- dry ashing
- wet ashing
- acid digestion
- fusion.

Dry ashing is widely used to decompose organic materials and to reduce the size of the sample. The concentrating effect allows lower limits of detection to be achieved. However, this method has several disadvantages the most serious of which is the loss of lead by volatilization or by plating onto metallic containers during the high-temperature ashing process due to the high volatility and ease of reduction of most lead compounds (189). A second disadvantage is that many tervalent and higher valent elements form refractory oxides and carbides while being heated under dry ashing conditions. Vigorous treatment of the ash is then required to ensure the complete conversion of these elements to the proper ionic states (190). A third disadvantage is that cross-contamination becomes a possibility when ashing containers are repeatedly used. Finally, corrosion of metallic containers and etching of silica or porcelain containers can introduce additional foreign impurities to the sample (191).

Wet ashing with nitric and sulfuric acids is often used to decompose biological samples. The use of concentrated perchloric acid (72%) for this purpose is discouraged because it is a very powerful oxidizing agent. However, it loses its oxidizing power when cooled and diluted. Therefore, one can moderate the oxidizing power of perchloric acid by controlling its concentration and the reaction temperature. For example, wet ashing — using an equal mixture of concentrated perchloric acid (72%) and concentrated nitric acid (60%) at 15–20°C — is no more vigorous than using concentrated nitric acid alone. The effect of the nitric acid is to oxidize the more reactive components at lower temperatures. As the reaction temperature is increased, the oxidizing power of perchloric acid increases gradually and reaches a maximum when nitric acid is completely evaporated.

Acid digestion is normally used to leach elements from solid samples, such as ores, sediments, and tailings. The divalent and tervalent elements, not bound up in acid insoluble particles, can frequently be leached successfully, but the higher valent elements are generally not quantitatively leached. If siliceous materials are present, recovery of even the lower valent elements will be markedly incomplete unless hydrofluoric acid is used.

An alternative to sample dissolution by acid digestion is *fusion with fluxes*, such as sodium peroxide, sodium carbonate, alkali pyrosulfate and anhydrous potassium fluoride. Sodium peroxide is a relatively corrosive flux. It also severely attacks the fusion container (silica, iron, nickel, zirconium, etc.) and, in that way, introduces additional quantities of impurities to the sample. Sodium carbonate fusion is cleaner but is relatively mild. The dissolution of refractory materials is incomplete.

Fusion with an alkali pyrosulfate flux is one of the most powerful, clean and convenient methods available for the dissolution of non-siliceous refractory materials. It is easily prepared by heating sodium or potassium sulfate with an equal molar quantity of concentrated sulfuric acid. The flux is virtually a molten acid. It loses sulfur trioxide on heating, with gradual increase in the melting point to nearly 800°C. This high reaction temperature, the high acid concentration and the high concentration of sulfate ion (acting as an inorganic complexing agent for metals) are responsible for its efficiency in dissolving refractory metallic oxides, carbides and sulfates. The pyrosulfate flux is also a powerful oxidizing agent and can decompose very resistant organic matter more rapidly and completely than perchloric acid.

Fusion with anhydrous potassium fluoride is probably the simplest, most reliable method available for the complete dissolution of all siliceous materials and metallic oxides. It is well known that fluoride ions form extremely stable inorganic complexes with many heavy metals. Therefore, the molten potassium fluoride not only provides the high concentration of fluoride ions but also the high temperature (846°C) for the chemical attack. In the presence of small amounts of nitrate, organic material and refractory carbides are oxidized smoothly and rapidly. After fusion, the cake is transposed with concentrated sulfuric acid to a completely clear pyrosulfate fusion. The silica and fluorides are eliminated simultaneously, as silicon tetrafluoride and hydrogen fluoride, by volatilization. The residue dissolves easily in dilute hydrochloric acid.

2.2 INTERFERENCES

Not applicable

2.3 APPARATUS

- Perchloric acid fumehood: Constructed of #316 stainless steel with wash-down capabilities to clean the blower, exhaust ducting and interior working area
- Hotplate: Teflon coated with 40-cm × 80-cm heating surface and 220°C maximum temperature; provides large surface for batch evaporation of water samples and safe temperature for digestions using Teflon TFE beakers
- Platinum dishes: 40 or 50 mL, approximately 50-mm diameter by 25-mm high
- Muffle furnace: Variable temperature control
- Ashing containers: Stainless steel, 500-mL
- Grinder
- Blast burner: Meker
- Crucible tongs: Platinum tipped (Engelhard 506)
- Flashlight
- Plastic stirring rods: 3-mm × 10-cm, round ends
- Teflon beakers: TFE, 100-mL
- Teflon watch glass: TFE, 50-mm diameter
- Miscellaneous glassware.

2.4 Reagents

- Barium-133 tracer: Dilute a stock solution to give 1×10^4 cpm/mL in 0.1 N HCl
- Bismuth-207 tracer: Dilute a stock solution to give 1×10^4 cpm/mL in 2 N HCl
- Thorium-234 tracer: Prepare from uranyl nitrate hexahydrate (192) or U_3O_8 (99) and dilute to give 1×10^4 cpm/mL in 4 M HNO_3
- Lead-bismuth carrier (1 mg each of lead and bismuth/mL): Dissolve 800 mg of $Pb(NO_3)_2$ and 1.16 g of $Bi(NO_3)\cdot 5H_2O$ in 2 N HCl and dilute to 500 mL
- Hydrochloric acid (12 N): Reagent grade
- Nitric acid (16 N): Reagent grade
- Hydrofluoric acid (50%): Reagent grade
- Perchloric acid (70%): Reagent grade
- Sulfuric acid (36 N): Reagent grade
- Potassium fluoride: Anhydrous, reagent grade
- Potassium sulfate: Anhydrous, reagent grade
- Sodium sulfate: Anhydrous, reagent grade
- Silica gel: Reagent grade.

2.5 PROCEDURES

The selection of sample decomposition procedures for various environmental samples is tabulated in Table 2. All procedures are detailed below. Procedures B to F, inclusive, have all been tested at the authors' laboratory and found to provide complete dissolution of all sample matrices. The final solutions are completely clear, free of insoluble material and are ready for radionuclide analysis.

2.5.1 Procedure A – Dry Ashing

Sample: Biological

Determination: Gross alpha, beta and gamma; or proceed to 2.5.4 (Procedure D).

1. Place a preweighed sample in the stainless steel ashing container.
2. Heat the sample in a muffle furnace at 125°C until dry. Break up the dried material with a spatula if necessary.
3. Increase the temperature to 250°C and hold for 4 h.
4. Increase the temperature to 400°C and hold for 4 h.
5. Increase the temperature to 500°C and hold for 10–15 h.
6. Remove the container from the furnace. Cool to room temperature and determine weight of ash.
7. Pulverize ash to less than 100 mesh.

Table 2. Selection of procedure for sample decomposition

Sample Matrix	Ra/Th	Pb
Aqueous* – No organic or insoluble material†	None required	None required
Aqueous* – presence of organic and/or less than 1 g of insoluble material per litre	Procedure C – evaporation, HNO_3/$HClO_4$/HF digestion and pyrosulfate fusion	Procedure B – evaporation and HNO_3/$HClO_4$/HF digestion
Aqueous* – presence of more than 1 g of insoluble material per litre	Separate the entire sample into an aqueous and a solid sample by filtering through a 3-μ membrane filter and treat each individually	
Solid – ore, sediment, soil, tailings, ash, air filter/dust, etc.	Procedure D – KF fusion and pyrosulfate fusion	Procedure E – HNO_3/$HClO_4$/HF digestion and pyrosulfate fusion
Biological	Procedure F – Wet ashing OR Procedure A – Dry ashing followed by Procedure D	Procedure F – Wet ashing

*For unacidified sample, add 5 mL of 12 N HCl per litre of sample, mix thoroughly and allow to stand for at least four hours.

†Mix container thoroughly and pour 500 mL into a 600-mL beaker. Turn off room lights, examine the solution by viewing downward through the top of the beaker while shining a flashlight obliquely upward through the bottom and sides. The solution should be colourless and clear.

2.5.2 Procedure B

Sample: Aqueous, containing organic material and/or less than 1 g/L of insoluble material.

Determination: Pb-210.

1. Mix sample vigorously and accurately transfer 500 mL to a 600-mL beaker.
2. Add 10 mL of 16 N HNO_3, 5 mL of 70% $HClO_4$, 1.0 mL of lead–bismuth carrier and 1.0 mL of Bi-207 tracer.
3. Evaporate to a volume of 10 mL in a perchloric acid fumehood.
4. Transfer the solution to a 100-mL Teflon TFE beaker and rinse with 5 mL of 16 N HNO_3.
5. Add 2 mL of 50% HF, cover with a Teflon watch glass and digest at 100°C until clear. Repeat HF treatment if necessary.
6. Remove watch glass and evaporate just to dryness.
   Note: Do not bake the residue.
7. Add 20 mL of 2 N HCl, mix and, if necessary, heat to dissolve all salts.
8. Cool, transfer to a 250-mL Erlenmeyer flask, dilute to 100 mL with 2 N HCl and proceed to Pb-210 determination.

2.5.3 Procedure C

Sample: Water, containing organic material and/or less than 1 g/L of insoluble material.

Determination: Ra-226, Ra-228, Th-228, Th-230, Th-232 and Total Thorium.

1. Mix sample vigorously and accurately transfer 500 mL to a 600-mL beaker.
   Note: For unacidified samples, add 5 mL of 12 N HCl per litre of sample, mix thoroughly and allow to stand for at least 5 h.
2. Add 1.0 mL each of Ba-133 and Th-234 tracers, 10 mL of 16 N HNO_3 and 5 mL of 70% $HClO_4$.
3. Evaporate to 10 mL in a perchloric acid fumehood.
4. Transfer the solution to a 100-mL Teflon TFE beaker and rinse with 5 mL of 16 N HNO_3.
5. Add 2 mL of 50% HF, cover with a Teflon watch glass and digest at 100°C until clear. Repeat HF treatment if necessary.
6. Remove watch glass and evaporate to perchloric acid fumes.
7. Rinse the walls with 5 mL of 36 N H_2SO_4, mix and continue the evaporation for 10–15 min at which time the solution rolls around the bottom of the beaker like a pool of mercury.
8. Carefully roll the solution around the sides to collect all isolated droplets and pour the solution into a 125-mL Erlenmeyer flask containing 2 g of anhydrous Na_2SO_4 and 5 g of anhydrous K_2SO_4.
9. Immediately evaporate the solution over a blast burner to a pyrosulfate fusion.
10. Dissolve the cake in 50 mL of 5% HCl with heating.
11. Transfer the clear solution to a 250-mL beaker, rinse the flask with 50 mL deionized water and add to the beaker.
12. Proceed to Ra-226, Ra-228, Th-228, Th-230, Th-232 or Total Thorium determinations.

2.5.4 Procedure D

Sample: Ore, sediment, soil, tailings, ash, air filter dust, etc.

Determination: Ra-226, Ra-228, Th-228, Th-230, Th-232 and Total Thorium.

1. Weigh 1.0 g of 100-mesh sample in a 40-mL platinum dish.
2. Wet sample with 0.5 mL of 16 N HNO_3, and warm gently at 100°C on a hotplate until the chemical reaction and frothing have ceased.
3. Add 1.0 mL each of Ba-133 and Th-234 tracers and evaporate just to dryness.
   Note: Do not bake!
4. Add 2 mL of 50% HF and evaporate just to dryness.
5. Sprinkle 3 g of anhydrous KF uniformly over the residue and mix with a plastic stirring rod.
6. Fuse over a blast burner until KF dissolves.
   Note: a) Takes approximately 4–7 min.
   b) If the melt is turbid or highly coloured, add 250 mg of pure silica gel and continue fusion to a clear melt.
7. With a pair of crucible tongs, grasp the outside walls of the dish and roll the melt around the upper walls.
   Note: The tips of crucible tongs should NEVER be in contact with the inside walls of the platinum dish.
8. Resume heating until a clear melt is obtained and continue for 2 min.
9. Cool to room temperature, add 4.5 mL of 36 N H_2SO_4 and warm gently on a hot plate until the KF fusion cake dissolves completely.
10. Heat over blast burner carefully until copious fumes of H_2SO_4 are evolved.
11. Add 2 g of anhydrous Na_2SO_4 and continue heating until a clear pyrosulfate melt is obtained.
12. Use crucible tongs to grasp the outside walls and roll the melt to the upper walls to dissolve any remaining particles.
13. Cool to room temperature, flex the walls to break loose the cake and place the cake in a 250-mL beaker.

14. Add 35 mL of boiling 5% HCl to the dish and leave it on the hot plate for a few minutes to dissolve any cake remaining in the dish. Roll solution carefully to reach the upper walls.
15. Pour the solution into the beaker containing the main portion of the fusion cake and place beaker on the hot plate.
16. Hold dish upside down, using a disposable pipette, rinse the inside walls with 15 mL of boiling 5% HCl, directly into the beaker. Make sure that hot rinses reach all parts of the inside walls by rotating the dish.
    Note: a) Use 'rubber fingers' to protect hands.
    b) The platinum dish should not be placed in the beaker.
17. Cover the beaker, boil and swirl to dissolve the cake completely.
18. Cool to room temperature and add 50 mL of deionized water.
19. Proceed to Ra-226, Ra-228, Th-228, Th-230, Th-232 and Total Thorium determinations.

2.5.5 Procedure E

Sample: Ore, tailings, soil, sediment, ash, air filter/dust, etc.

Determination: Pb-210.

1. Weigh 1.0 g of 100-mesh sample or an air filter into a 100-mL Teflon TFE beaker.
2. Add 5 mL each of 16 N HNO_3 and 50% HF, 2 mL of 70% $HClO_4$, 1.0 mL of lead–bismuth carrier and 1.0 mL of Bi-207 tracer and cover with a Teflon watch glass.
    Note: a) For glass-fibre filters greater than 5 cm, dissolve the filter with HF first.
    b) For cellulose filters greater than 5 cm, digest at room temperature initially and slowly increase temperature.
3. In a perchloric acid fumehood, digest at 100°C until sample dissolves.
4. Remove watch glass and evaporate to perchloric acid fumes.
5. Wash down the walls with 5 mL of 36 N H_2SO_4, mix and fume for 10–15 min.
6. Roll the solution around to collect isolated droplets and pour into a 250-mL Erlenmeyer flask containing 2 g of anhydrous Na_2SO_4 and 5 g of anhydrous K_2SO_4.
7. Quickly evaporate over a blast burner to a clear pyrosulfate melt. Cool.
8. Add 20 mL of boiling 3 N HCl, swirl and boil for 5 min. Cool.
9. Add 50 mL of 3 N HCl and 35 mL of deionized water to a final volume of 105 mL in 2 N HCl and proceed to Pb-210 determination.

2.5.6 Procedure F

Sample: Biological samples.

Determination: Ra-226, Ra-228, Th-228, Th-230, Th-232, Total Thorium and Pb-210.

WARNING: Because of the potentially explosive nature of perchloric acid digestions, all persons using this acid should be thoroughly familiar with its hazards (193–195). Some safety practices are:

- all work must be done in a fumehood designed for perchloric acid;
- use goggles, barrier shields and other devices as necessary for personal protection;
- never add sample to concentrated (>60%) perchloric acid;
- avoid use of organic chemicals/solvents in perchloric acid fumehood;
- remove spilled acid by immediately and thoroughly washing with large amounts of water.

1. Weigh 10 g of sample into a 250-mL beaker.
2. Add 50 mL of 1:1 mixture of 16 N HNO_3 and 70% $HClO_4$, 1.0 mL each of Ba-133 and Th-234 tracers.
    Note: Digest a separate sample for Pb-210, adding 1.0 mL each of lead–bismuth carrier and Bi-207 tracer.
3. Digest at room temperature, in a perchloric acid fumehood, until frothing subsides.
    Note: Be prepared to moderate the reaction by cooling in a cold water bath.
4. Place the beaker, with cover, on a hot plate. Raise digestion temperature in 20° increments to a maximum of 120°C and continue digestion until the solution clears.
5. Remove cover. Evaporate just to dryness and cool to room temperature.
6. Add 10 mL of boiling 3 N HCl. Swirl and boil for 5 min.
7. Add 50 mL of 5% H_2SO_4, 5 g of anhydrous Na_2SO_4 and 40 mL of deionized water. Mix thoroughly and proceed to Ra-226, Ra-228, Th-228, Th-230, Th-232 and Total Thorium determinations.
    Note: Transfer the digestion for Pb-210 to a 250-mL Erlenmeyer flask, add 60 mL of 3 N HCl and 35 mL of deionized water to give a final volume of 105 mL in 2 N HCl and proceed to Pb-210 determination.

3. GROSS ALPHA AND BETA MEASUREMENTS

3.1 PRINCIPLE

This method covers the determination of gross alpha and gross beta activities in water, sediments, tailings, air particulates and biological samples. Gross alpha includes alpha emitters having energies greater than 3.9 MeV and gross beta encompasses beta emitters having energies between 0.1 and 3.9 MeV (196–202).

In this method, solids, filters, residues from the evaporation of water, and ash from the dry ashing of biological samples are counted directly. Since the counting of both alpha and beta emitters is very much influenced by self-absorption, the size of the sample is an important consideration. The maximum sample size is determined by the area of the planchet (usually 5-cm diameter) and the maximum thickness, above which unacceptable self-absorption occurs. For alpha particles of about 5 MeV energy 5 mg/cm^2 is the limiting thickness, whereas for betas of about 1 MeV the thickness may be increased to about 25 mg/cm^2. When both alphas and betas are being measured in the same sample, the sample size will be limited to about 100 mg (for 5-cm diameter planchets).

Radionuclides that are volatile under the sample preparation conditions of this method will, of course, not be included in the gross measurements.

Gross alpha and beta measurements do not provide information on the energy distribution of the detected radiation. In the case of samples containing several radionuclides that may or may not have reached radioactive equilibrium with their daughters, the measurements may be difficult to interpret. This method, however, may be valuable as a quick assessment of samples containing sufficient activity to justify more detailed study.

Any detector responding to loss of energy by ionization can, in principle, be used for gross alpha/beta measurements providing the particles can penetrate the window of the detector. A Geiger counter with a thin mica window would be the simplest and cheapest type of detector. In these counters the output pulse has the same amplitude irrespective of the amount of ionization loss suffered by the incoming particles in the detector, and, therefore, alphas and betas cannot be distinguished. Counts resulting from each type of radiation could, in principle, be separated by placing absorption foils of different thicknesses over the sample and thus determining the range of the radiation emitted. This procedure is too time-consuming if a quick determination of gross alpha and beta activities is needed.

Commercially available instruments for gross alpha and beta measurements consist of two main varieties:

- continuous flow proportional chambers
- dual scintillation detectors (phoswich).

The major cost of these instruments is in the shielding required to reduce the background from external radiation (cosmic rays, gammas from the decay of radon in the air, etc.). Most instruments contain active and passive shielding. In the phoswich detector, the alpha/beta detector is surrounded by a guard detector which signals the passage of external radiation and, by means of anti-coincidence circuitry, prevents it being counted. The passive shielding consists of an enclosure of several centimetres thickness of aged lead. The lead shield may also be a large fraction of the cost of the instrument.

The *continuous flow proportional counter* consists of a chamber containing counting gas (a mixture of argon and methane) in which a small-diameter anode (wire or point) is surrounded by a cylindrical cathode. Electrons liberated from atoms of the counting gas by the passage of ionizing radiation are collected at the anode. The electrical pulse, produced across a resistor in series with the anode, has an amplitude proportional to the ionization produced by the particle absorbed in the detector. In order to maintain this proportional behaviour, the counter gas must be replenished continuously. In commercial instruments, the flow of counting gas is regulated by an automatic regulator at a flowrate of about 100 mL/min.

Commercial instruments usually contain two 'pancake' counters mounted close together. The lower counter has a window (80-500 μg/cm^2) under which the sample is placed for counting. The upper counter is operated in the anti-coincidence mode, i.e., eliminating counts resulting from particles or gamma rays that penetrate both detectors. The entire assembly is usually surrounded by about ten centimetres (four inches) of lead shielding.

The proportional counter is relatively insensitive to gamma radiation and provides good discrimination between alpha and beta particles. Since ionization loss (dE/dx) is measured rather than total energy, the output of the counter provides a pulse height spectrum of poor energy resolution. Despite this drawback, gas flow proportional counter instruments require fairly simple electronic circuitry which provides adequate discrimination between alphas and betas.

Commercial instruments are available with electrically operated sample changers which permit several samples to be counted unattended.

In the solid state *scintillation detector*, a thin slice of scintillator of relatively low atomic number, e.g., CaF_2, is used to detect alphas and betas. The light emitted is recorded by a photomultiplier. A second,

thicker piece of scintillator, usually NaI, is used to signal the passage of external radiation. Because of the different decay times of the light emitted by the two scintillators, it is possible to use a sandwich of the two with a single photomultiplier (hence the name "phoswich" derived from phosphor sandwich). The composite electrical signal from the anode of the photomultiplier is sorted out by pulse shape discrimination circuitry, to produce two signals deriving from each scintillator that are then routed to electronic logic. Gross alpha/beta instruments using phoswich detectors tend to be more compact than the flow-through proportional counter types, but require more electronic circuitry (usually provided as a number of NIM modules). The sample is placed close to the scintillation counter and a geometric factor of about 0.3 is usual. A thin, aluminized Mylar window must be placed between the sample and the scintillator to prevent light from entering. This window has a negligible effect on count rates except for very low-energy alpha particles arriving after passage through thicker parts of the sample. The intrinsic efficiency of the phoswich detector for alphas and betas is close to 100% because of the high absorptivity of the solid scintillator.

In some decay schemes, the alpha or beta decay of a radionuclide results in a daughter which undergoes prompt gamma decay. For anticoincident counting this can result in some fraction of the activity being automatically rejected by the guard counter. A second measurement with the counter in the coincident mode can be used to determine this fraction.

Gross alpha/beta instruments must be regularly calibrated to ensure that instrument settings are correct for the proper separation of alpha and beta events and the rejection of penetrating events (gammas, cosmic rays). Extended sources (in the sense that the activity is deposited uniformly over the planchet) of alpha and beta emitters, such as americium-241 and strontium-90, are used for calibration. The output of the detector is examined with a multichannel analyzer and the various preset controls (high voltage, discriminators) are adjusted according to the manufacturer's instructions. Alpha-beta crosstalk (i.e., alphas contributing to the beta count and vice versa) is usually a few per cent except for rare combinations of sources emitting high-energy betas ($\geq$1.5 MeV) and low-energy alphas ($\leq$4.5 MeV). If such combinations are suspected in samples, the output should be examined with a multichannel analyzer.

Alpha particles have well-defined ranges. For energies of a few MeV, the range is a few milligrams per square centimetre, and varies approximately as energy to the power 1.5. Beta particles undergo multiple scattering and are absorbed with source thickness according to an approximate exponential law.

When the activities per unit mass of the sample are required, two approaches are possible.

a) The sample is compared with a standard source of identical geometry and thickness (as expressed in terms of the range of the activity in question). Standards can be made by incorporating known activity into a matrix that simulates the matrix of the sample being measured: that is, by coprecipitation in a compound of similar density and chemical composition. Examples are, radium-226 in $BaSO_4$ and lead-210 in $PbSO_4$.

b) An attempt can be made to derive an absolute activity by accounting for the geometric factor and the absorption of some of the particles within the source (especially those moving obliquely through the source). Since range is a function of energy, the self-absorption correction for each nuclide will depend on its emitted energy. A correction must be made for the back-scattering of betas from the planchet. Alpha particle ranges are tabulated for several elements in reference books, and ranges in chemical compounds can be derived by taking a mean of the atomic ranges weighted by the mass fraction in a given compound. The magnitude of the self-absorption correction for alphas varies with the geometric factor. When the source is far away from the detector, only those particles moving vertically up will be collected, whereas those moving at large angles to the vertical, thus passing through more material in the source, can reach the detector when the source is close. Since most alpha-beta instruments have a geometric factor around 0.3, it may be noted that a source which is one half of the range thickness will have an 'effective' geometric factor (corrected for self-absorption) of about 0.27 (about 10% reduction).

   As the sample is moved closer and closer to a planar detector, the self-absorption correction becomes even more significant, so that in a nearly 2π geometry (rarely achieved in practice), the geometric factor of 0.5 is reduced to about 0.38 (a reduction of nearly 25%). Graphs showing the required correction for self-absorption for disc sources as a function of source-detector separation and source thickness have been published (196).

If a large number of samples of similar composition is to be measured, the analyst should determine an empirical correction for self-absorption by preparing a series of sources of different thicknesses from the same sample. In the absence of self-absorption, the count rate should be proportional to the mass of the sample. Thus, a line drawn through the origin

to an experimental point for a very thin source (e.g., one tenth of the range equivalent) predicts the behaviour in the absence of self-absorption. The count rate for a thicker source will generally fall below this line and the difference is a measure of the correction required for self-absorption. This technique assumes a count rate high enough to give good counting statistics.

The correction for back scatter may be estimated by comparing the count rate for an identical source contained in a low-Z material planchet of negligible mass (e.g., polystyrene) with the count rate obtained under identical geometry in a regular stainless steel planchet.

3.2 INTERFERENCES

Natural background contributions give a positive bias.

3.3 APPARATUS

- Counting systems: Low-background alpha and beta counter
- Counting planchets: Stainless steel to fit counting system used
- Electric hot plate
- Drying oven
- Infrared heat lamp
- Desiccator
- Vortex mixer.

3.4 REAGENTS

- Americium-241: NBS or NBS-traceable
- Strontium-90: NBS or NBS-traceable
- Acetone: Reagent grade
- Nitric acid (5%): Dilute 5 mL conc. HNO_3 to 100 mL with deionized water
- Acetone-glue: Dissolve 10 drops of cellulose-acetone glue in 100 mL acetone
- Lead nitrate solution (3.2%): Dissolve 32 g of $Pb(NO_3)_2$ in deionized water and dilute to 1 L
- Lead sulfate wash solution: Dissolve 50 g of K_2SO_4 in 1 L of 0.5% H_2SO_4.

3.5 PROCEDURES

3.5.1 Water

1. Evaporate to dryness an aliquot of sample acidified with HNO_3 in a preweighed borosilicate beaker or porcelain evaporation dish and determine weight of residue.
2. Rinse down the sides of the beaker with 10 mL of concentrated HNO_3, cover with a watch glass and evaporate to 1–2 mL.
3. Add 10 mL of 1 M HNO_3. Mix well.
4. Transfer an aliquot equivalent to 100 mg of the residue to a preweighed 5-cm stainless steel planchet. Evaporate to dryness under an infrared heat lamp and flame to a dull-red heat with a Meker burner. This will greatly increase the removal of gaseous and volatile radionuclides.
5. Determine the weight of residue in the planchet.
6. Store the planchet in a desiccator until ready for counting.

3.5.2 Tailings, soils, sediments, plant tissues and ashes

1. Place a planchet in a level position.
2. Weigh 100 mg of the sample into a 16-mm × 100-mm disposable test tube. Add 4 mL acetone-glue solution.
3. Mix vigorously with a vortex mixer and immediately pour into the planchet. Complete the transfer with an additional 1 mL of acetone-glue solution.
4. Evaporate acetone using an infrared heat lamp and store in desiccator until ready for counting.

3.5.3 Fish and other biological samples

1. Dry ash according to Procedure A (Section 2.5.1).
2. Follow all steps of 3.5.2 (above).

3.5.4 Air filter

1. Glue air filter (5-cm diameter or smaller) on planchet and proceed to counting. Digest larger filter using $HNO_3/HClO_4/HF$ and pyrosulfate fusion (Procedure E, Section 2.5.5) with one minor change. Dissolve the pyrosulfate fusion cake in 50 mL of 0.5% HCl.
2. Cool the solution to room temperature. Add 1 mL of 36 N H_2SO_4, 3 g of Na_2SO_4 and stir vigorously with a magnetic stirrer. Inject four 0.5-mL aliquots of a 3.2% $Pb(NO_3)_2$ solution. Allow 5 min to pass between aliquots. Add two additional 0.5-mL aliquots dropwise. Stir for 30 min.
3. Filter the $PbSO_4$ precipitate onto a 0.8-μ membrane filter and wash with 10 mL of lead sulfate wash.
4. Dry and glue filter onto planchet.

3.5.5 Gross alpha and gross beta measurement

1. Adjust the gross alpha/beta analyzer to the manufacturer's instructions for energy discrimination.
2. Place a standard Am-241 source of known alpha activity, A_α, in the sample chamber and determine the gross alpha count rate, r_α. Remove, and insert a standard Sr-90 source of known beta activity, A_β. Determine the gross beta count rate, r_β. With an empty sample chamber determine the gross alpha and beta background count rates, b_α and b_β, respectively.

3. Place the sample source of known weight, W, in the sample chamber and determine the gross alpha count rate, R_α, and the gross beta count rate, R_β.

3.6 CALCULATION

1. Calculate the gross alpha calibration constant, F_α, of the detector from the equation:

$$F_\alpha = \frac{r_\alpha - b_\alpha}{A_\alpha}.$$

2. Calculate the gross beta calibration constant, F_β, of the detector from the equation:

$$F_\beta = \frac{r_\beta - b_\beta}{A_\beta}.$$

3. Calculate the gross alpha, G_α, and gross beta, G_β, contents of the sample (Bq/g) from the equations:

$$G_\alpha = \frac{R_\alpha - b_\alpha}{F_\alpha W}$$

$$\text{and} \quad G_\beta = \frac{R_\beta - b_\beta}{F_\beta W}.$$

4. Calculate the counting precisions, σG_α and σG_β, of both measurements according to the equations:

$$\sigma G_i = G_i \times \left[\frac{(\sigma R_i)^2 + (\sigma b_i)^2}{(R_i - b_i)^2} + \frac{(\sigma r_i)^2 + (\sigma b_i)^2}{(r_i - b_i)^2} \right]^{0.5}$$

where:

$$i = \alpha \text{ or } \beta$$

and: $(\sigma y_i)^2 = y_i / t_{y_i}$,

where the symbol y_i represents the appropriate count rate (R_i, b_i or r_i) determined from the counts in the period t_{y_i}.

3.7 PRECISION

There are several factors that influence the overall precisions of the gross alpha and gross beta measurements. In addition to counting precision, they include sample homogeneity, reproducibility of sample positioning in the counting chamber, precision of weighing and volume measurements, timing errors and instrumental dead time errors. For samples whose activities are low and for which fewer than 100 counts are accumulated, the counting precision will usually be the largest contributor to the overall precision. For samples whose activities are high and for which greater than 10 000 counts are accumulated, the contribution of counting statistics will be negligible.

The magnitude of the contribution of procedural uncertainty should be assessed and combined with the counting precision in estimating a reportable overall precision of the measurement (see Appendix A).

4. GAMMA RAY SPECTROSCOPY

Gamma ray spectroscopy is mainly used to determine the activity of individual gamma emitters. In radiochemical procedures for determination of specific alpha and beta emitters, gamma emitting tracers can be added at the start of analysis and the recovery in the final source determined by gamma spectroscopy; for example, barium-133 in the determination of radium-226 and bismuth-207 in the determination of lead-210. Gamma ray spectroscopy may also be used to estimate the gross gamma activity of samples.

Gamma ray detectors that are commercially available consist of three main types:

1. Scintillometers: these consist of inorganic crystals such as NaI(Tl) and CsI(Tl) coupled to photomultipliers.
2. Lithium-drifted germanium detectors (Ge(Li)): in which a solid-state detector is maintained permanently at liquid nitrogen temperatures. Failure to maintain low temperatures will destroy this detector.
3. Hyperpure germanium detectors: similar to type 2 except that they only require cooling to liquid nitrogen temperatures for a few hours before use. These detectors can warm up to room temperature without permanent damage occurring.

Scintillation detectors (type 1) offer resolutions of between 20–60 KeV (FWHM) and efficiencies approaching 100% at lower energies (400 KeV). The cost depends on the size of the crystal and whether a straightforward cylindrical geometry as opposed to a well configuration is required. Costs are typically in the order of several hundred dollars.

The solid-state detectors (types 2 and 3) offer much higher resolution than scintillometers (typically 2 KeV at 1 MeV). The efficiency is about 70% of that of a similar-sized NaI(Tl) crystal. Costs are high ($10 000 – $20 000 in 1984), a supply of liquid nitrogen is required, and modern solid-state electronics are recommended. This is the only detector which allows accurate multi-radionuclide analysis without chemical separation.

4.1 TRACER MEASUREMENT

4.1.1 Principle

The gamma ray spectrometer is energy calibrated by exposing the detector to the radiation of several standard gamma sources emitting radiation at suitable energies, e.g., cobalt-57, cesium-137, cobalt-60 and yttrium-88. The detector output is usually examined with a multichannel analyzer where the position of the photopeak for each radionuclide (expressed as channel number) may be correlated against energy in order to check linearity. If a multichannel analyzer is not available, a spectrum of the photopeaks may be derived by incrementing the window of a single channel analyzer and recording the count rate at each setting. If routine measurements are only concerned with a few standard gamma ray emitters, the discriminator window may be set to the desired photopeak and the counts accumulated in the electronic counter.

The source itself should be of a standard geometry and preferably small compared with the sensitive volume of the detector. Normally, absorption within the source is negligible for sample thickness of a few grams per square centimetre. Shielding, in the form of lead bricks, is usually required to reduce background to suitable levels. Background is measured with an empty sample chamber.

4.1.2 Interferences

In tracer measurements, a high activity of tracer is added to minimize counting time and interferences from gamma emitters present in the sample. Spectral interference may arise if the same photopeak energy is present in both the sample and the tracer at comparable activities.

4.1.3 Apparatus

- Gamma ray detector
- Stabilized high-voltage supply (1–5 Kv depending on detector)
- Preamplifier
- Main amplifier
- Single-channel analyzer
- Scaler-counter
- Multichannel analyzer (optional): 1024 channel.

4.1.4 Reagents

- Standard gamma emitting sources: radium-226, cerium-141, chromium-51, cesium-137 and cobalt-60.

4.1.5 Procedures

1. In Chapter 2, the addition of chemical yield tracers to samples is described. Two of these gamma emitters, Ba-133 and Bi-207, are added to samples in amounts totalling 10^4 cpm (counts per minute) each. The preparation of the sample source containing Ba-133 tracer is described in Section 5.1.5. The procedure for preparation of the standard Ba-133 source is described in steps 16 to 21 of Section 5.1.5. The preparation of the sample source containing Bi-207 tracer is described in Section 7.5. The procedure for preparation of the standard Bi-207 source is described in step 20 of that section.

2. Determine the relationship between the multichannel analyzer channel number and energy by placing sources of different energies on the detector. Some suggested sources are Ra-226 (0.35, 0.61, 1.12 and 1.76 MeV), Ce-141 (0.14 MeV), Cr-51 (0.32 MeV) and Cs-137 (0.66 MeV).
3. Place the sample source containing the gamma-emitting tracer of interest on the detector. From the calibration in step 2 establish the appropriate energy window. Determine the gamma count rate, R_t, obtained in that window.
4. Using the same procedure determine the background count rate, b_t, with no sample on the detector.

4.1.6 Calculation

The only calculation required is to determine the count rate from the measurement of total counts accumulated in a specified period of time. Correct for background contribution.

$$R_t' = R_t - b_t.$$

4.1.7 Precision

Precision of the count rate measurement, $\sigma R_t'$, is solely a function of the counting statistics. It can be expressed as:

$$\sigma R_t' = \left[(\sigma R_t)^2 + (\sigma b_t)^2 \right]^{0.5}.$$

where:

$$(\sigma R_t)^2 = R_t/t_R$$
$$(\sigma b_t)^2 = b_t/t_b$$

and t_R and t_b are the measurement periods for the count rate determinations.

4.2 GROSS GAMMA MEASUREMENT

4.2.1 Principle

Gross gamma activity or activity of individual gamma ray emitting radionuclides is determined by counting a standard source (having the same geometry and mass distribution as the sample) and comparing its count rate with that of the sample. Gross gamma measurement is rarely required as a standard radiometric procedure since the results are difficult to interpret. However, these measurements are easily done by setting a suitable energy window from well above the noise level (typically around 100 KeV) to a high energy above which there is unlikely to be any gamma ray emissions (typically around 2.7 MeV). Like gross alpha and gross beta tests, gross gamma measurement is a preliminary test to sort out the most active samples and give some idea of their activity levels.

4.2.2 Interferences

With instruments where the detector is adequately shielded, there are no significant interferences.

4.2.3 Apparatus

See Section 4.1.3.

4.2.4 Reagents

- Standard cesium-137 source: Of known gamma activity and having the same geometry and mass distribution as the sample
- Gamma emitting sources: radium-226, cerium-141, chromium-51, cesium-137 and cobalt-60.

4.2.5 Procedures

1. Determine the relationship between the multichannel analyzer channel number and gamma energy using the procedure described in step 2 of Section 4.1.5.
2. Place the Cs-137 source on the detector. From the calibration in step 1 above, establish the energy window for Cs-137.
3. Calculate the instrument calibration constant, F, by comparing the observed count rate, r, with the known activity, in Bq, of the standard, A_s.

$$F = \frac{r - b}{A_s}$$

where:

b = background count rate with no sample on the detector.

4. Transfer a known weight, W (10–20 gm), of sample to a plastic container. For liquids, transfer a known volume to a Marinelli beaker.
5. Set the energy window to include the range from 100 KeV to 2.8 MeV.
6. Count for a period suitable for obtaining the desired counting precision. Calculate the gross gamma count rate, R. Determine the gross gamma background count rate, B, with no sample on the detector.
7. Calculate the gross gamma activity, G_γ, of the sample and report it in terms of equivalent Cs-137 activity (Bq/g or Bq/L) using the equation:

$$G_\gamma = \frac{R - B}{FW}.$$

8. Calculate the counting precision of the gross gamma measurement, σG_γ, from the equation:

$$\sigma G_\gamma = G_\gamma \times \left[\frac{(\sigma R)^2 + (\sigma B)^2}{(R - B)^2} + \frac{(\sigma r)^2 + (\sigma b)^2}{(r - b)^2} \right]^{0.5}$$

where:

$$(\sigma y)^2 = y/t_y$$

and the symbol y represents the appropriate count rate (R, B, r or b) determined from the counts in the period t_y.

4.2.6 Precision

The precision and accuracy of the method is influenced by σG and the number and energy of the gamma emitters present. This is so because the counting efficiency is a function of the gamma energy. The gross gamma activity obtained is also dependent on the relative amounts of the different gamma emitters present and is not necessarily simply proportional to the total activity present. Consequently its use should be restricted to relative measurements between samples of the same type.

5. DETERMINATION OF RADIUM-226

For the determination of radium-226, two radiochemical methods have been chosen. They are alpha spectroscopy and radon emanation. The first requires alpha spectroscopy capabilities and the second requires ZnS scintillation cells and a scintillation counter.

5.1 ALPHA SPECTROSCOPY METHOD

5.1.1 Principle

All radium isotopes, together with actinide and lanthanide elements, are separated from the gross sample constituents by coprecipitation with lead sulfate. After dissolving the latter in either alkaline ethylenediaminetetraacetic acid or alkaline diethylenetriaminepentaacetic acid, radium isotopes are then separated from the others by coprecipitation with barium sulfate at pH 4.8. The alpha spectrum of this source allows radium-226 to be determined unambiguously whereas the energies of radium-223 and radium-224 overlap resulting in a composite peak. The radium-223 contribution to the composite peak is equal to the polonium-215 peak at 7.38 MeV. The very short half-lives of radon-219 (4 s) and polonium-215 (1.8 ms) ensure that polonium-215 is in equilibrium with radium-223.

5.1.2 Interferences

There are no elemental or isotopic interferences in the analysis of radium-226 by this method. The major problem that may be encountered is that of poor spectral resolution. This may occur if the barium sulfate is not distributed in a thin, uniform layer or if the mass of the source becomes too large. The resulting loss in resolution may cause the low-energy tail of the radon-222 peak to spill into the radium-226 peak. This of course can only occur after ingrowth of radon-222. Counting samples as soon after preparation as possible will minimize this effect.

5.1.3 Apparatus

- Alpha spectrometer: Surface barrier or silicon-diffused junction detectors, preamplifier, bias voltage supply, linear amplifier, multichannel analyzer
- Gamma counting system: NaI crystal, power supply, pulse height analyzer
- Vortex mixer
- Syringes: Disposable, 3- or 5-mL capacity
- Micropipettes: 100- and 200-µL and 1.0-mL with disposable tips
- Centrifuge
- Filter holder: Conical, for 25-mm filter with stainless steel support screen
- Membrane filter: Cellulose acetate, 25-mm diameter, 0.2-µ pores
- Centrifuge tubes: Conical, 40-mL capacity
- Plastic discs: 25-mm diameter × 2-mm.

5.1.4 Reagents

- Barium solution (1 mg of Ba per mL): Dilute 20 mL of a 5-mg Ba per mL solution to 100 mL with deionized water
- Sodium sulfate solution (40% w/v): Dissolve 400 g of anhydrous Na_2SO_4 in deionized water and make up to 1 L
- Lead nitrate solution (3.2%): Dissolve 32 g of $Pb(NO_3)_2$ in deionized water and dilute to 1 L
- Lead sulfate wash solution: Dissolve 50 g of K_2SO_4 in 1 L of 0.5% H_2SO_4
- Alkaline DTPA (0.2 M and 0.5 M): Dissolve 38 g of NaOH in 800 mL of deionized water and add 80 g of diethylenetriaminepentaacetic acid while stirring. Cool, adjust pH to 10.6 with 10 N NaOH and dilute to 1 L with water. Prepare 100 mL of 0.5 M using 9.5 g of NaOH and 20 g of DTPA
- Sodium hydroxide solution (10 N): Dissolve 400 g NaOH in deionized water and make up to 1 L
- Sulfuric acid (36 N): Reagent grade
- Potassium sulfate: Anhydrous, reagent grade
- Seeding suspension (0.125 mg/mL of Ba): Place 11.3 mg of $BaCl_2 \cdot 2H_2O$, 10 mL of a 70% sodium hydrogen sulfate solution, and one drop of 72% perchloric acid into a 250-mL Erlenmeyer flask. Evaporate the solution carefully over a blast burner, swirling the solution continuously to prevent bumping, until the barium sulfate has dissolved. Increase the heating and continue until most of the excess sulfuric acid has been expelled and a pyrosulfate fusion is obtained. Cool the flask, while rolling the melt around the sides so that the cake is deposited on the sides as uniformly as possible to facilitate subsequent dissolution. Cool the flask and contents to room temperature. Add 25 mL of 40% sodium sulfate solution and 25 mL of deionized water. Swirl continuously until the cake is completely dissolved. For the best alpha spectrum resolution, prepare this suspension the day it is to be used. However, for most practical work, the suspension can be used almost indefinitely. Shake vigorously or place in an ultrasonic bath for a few minutes before use if not freshly prepared.
- Sodium sulfate–acetic acid: Mix 50 mL of 40% sodium sulfate solution with 4 mL of glacial acetic acid
- Radium-226 standard solution (4 Bq per mL): Dilute NBS traceable radium-226 in 0.1 N HCl
- Barium-133: See Chapter 2.

5.1.5 Procedures

1. To the prepared sample solution (Procedure C, D or F, Sections 2.5.3, 2.5.4 and 2.5.6 respectively) at room temperature, inject three 1-mL aliquots of a 3.2% $Pb(NO_3)_2$ while stirring vigorously. Allow 5 min between aliquots. Add two additional 1-mL aliquots dropwise. Keep stirring for 30 min. For a clear aqueous sample, transfer 1000 mL to a 1500-mL beaker. Add 1.0 mL of Ba-133 (also 1.0 mL of Th-234 if thorium determination is required), 20 mL of 36 N H_2SO_4 and 40 g of K_2SO_4 and mix. Inject five 1-mL aliquots of a 3.2% $Pb(NO_3)_2$ into the solution with vigorous stirring. Allow 5 min between aliquots. Add two additional 1-mL aliquots, dropwise. Keep stirring for 30 min.
2. Allow to stand for 4 h or more. Carefully decant most of the supernatant.
3. Swirl to suspend the precipitate and transfer to a 40-mL conical centrifuge tube with the aid of a sulfate wash solution.
4. Centrifuge at 2000 rpm for 10 min. Decant the supernatant.
5. Using a 5-mL disposable syringe, with the tip directly on top of the tightly packed precipitate, inject 5 mL of the sulfate wash solution to disperse it. Mix thoroughly using a vortex mixer and rinse the walls with 2 mL of the sulfate wash solution.
6. Centrifuge and decant the wash solution.
7. Disperse the precipitate by injecting 5 mL of a 0.2 M alkaline DTPA solution. Mix using a vortex mixer and heat in a hot water bath until the precipitate dissolves. It should be free of any turbidity when examined with a flashlight in a darkened room.
8. If the solution is turbid and the pH is below 9, add a drop of 10 N NaOH. If the solution is turbid and the pH is above 9, add 50-µL aliquots of a 0.5 M alkaline DTPA until the solution clears.
9. Cool in a cold water bath. Add 0.1 mL of the 1 mg/mL barium solution.
10. Using a syringe, rapidly inject 3 mL of the mixed Na_2SO_4/acetic acid solution into the solution. Immediately add 0.2 mL of the seeding suspension from a micropipette and mix using the vortex mixer. A turbidity much greater than that present in the seeding suspension forms instantly and reaches its maximum intensity within 1 min. Allow to cool for 30 min.

    Note: The syringe and the micropipette should be prefilled and mounted side by side on a stand to allow the addition of seeding suspension within two seconds of the injection.

11. Mix the content of the centrifuge tube using the vortex mixer. Pour the content onto a 25-mm 0.2-µ membrane filter and while holding the centrifuge tube in the pouring position, rinse the interior with 2–3 mL of sulfate wash solution from a wash bottle. Rinse the sides of the filter holder with 2–3 mL of sulfate wash solution in a circular motion just above the previous aqueous level.

    Note: Collect the filtrate in a clean test tube and save for thorium determination, if required.

12. Glue the membrane filter onto a plastic disc for alpha spectrometric determination of Ra-226 (Ra-223 and Ra-224 may be determined indirectly through their respective polonium daughters) and gamma counting of the tracer Ba-133 for yield measurement (described in Chapter 4).
13. Place the sample source in the alpha spectrometer and record the alpha particle spectrum on the multichannel analyzer. Depending on the source thickness, the activities of the radium isotopes present and the age of the source, the spectrum should be similar to that shown in Figure 2. A radium isotope spectrum obtained using Elliot Lake uranium mill tailings is shown in Figure 3. It shows the presence of the other radium isotopes, Ra-224 and Ra-223. Consequently, it is more complicated than the spectrum of Ra-226 alone.
14. Count for a sufficient length of time to prevent counting statistics becoming a significant source of error. Calculate the count rate, R. Remove the sample from the alpha spectrometer as soon as possible in order to minimize contamination of the detector with Rn-222 recoil. This problem can be minimized by equipping the spectrometer with pressure and voltage regulating devices (203).
15. Determine the Ba-133 gamma count rate, R_t, for the sample source (described in Chapter 4).
16. Prepare a calibration source by placing an exact activity, A_s (Bq), of the standard Ra-226 solution and 100 µL of the barium solution into a conical centrifuge tube. Add an activity of Ba-133 identical to that employed for samples at the decomposition stage (see Chapter 2) or at step 1 above. Precipitate as barium sulfate, filter and prepare the source in the manner described in steps 1–12 above.
17. Count the radium calibration source in the alpha spectrometer under the same conditions used for the sample source. Record the count rate, r, for Ra-226.
18. Determine the Ba-133 gamma count rate, r_t, for the standard source (described in Chapter 4).

19. Prepare a blank reagent source in the same manner as the calibration source.
20. Count the blank source in the alpha spectrometer under the same conditions used for the calibration source. Record the count rate, b, for Ra-226.
21. Determine the Ba-133 gamma count rate, b_t, for the blank source (described in Chapter 4).

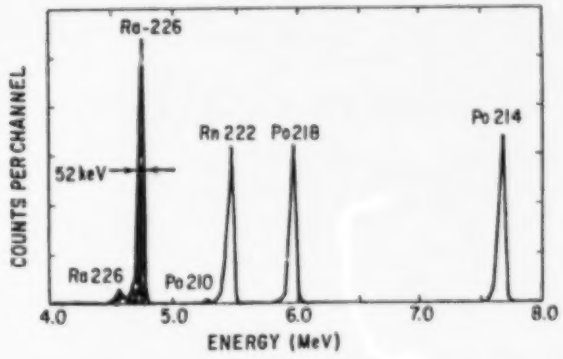

Fig. 2 – Alpha spectrum of Ra-226 and daughters in barium sulfate. Shaded curve, obtained immediately after separation; open curve, daughters ingrown after 29 d (41).

5.1.6 Calculations

1. Calculate the apparent calibration constant from the equation:

$$F = \frac{r - b}{A_s}.$$

2. Calculate the relative chemical yield factor, Y, the recovery of the sample source relative to the recovery of the calibration source, from the equation:

$$Y = \frac{R_t - b_t}{r_t - b_t}.$$

3. Calculate the Ra-226 alpha activity of the sample, A (Bq/g), according to the equation:

$$A = \frac{R - b}{F\,Y\,W}.$$

where:

W is the weight (in grams) of the solid sample originally taken. In the case of liquid samples, W may represent volume (litres).

4. Calculate the radiometric counting precision, σA, of the Ra-226 measurement according to the equation:

$$\sigma A = A \times \left[\frac{(\sigma R)^2 + (\sigma b)^2}{(R - b)^2} + \frac{(\sigma r)^2 + (\sigma b)^2}{(r - b)^2} + \frac{(\sigma Y)^2}{Y^2} \right]^{0.5}$$

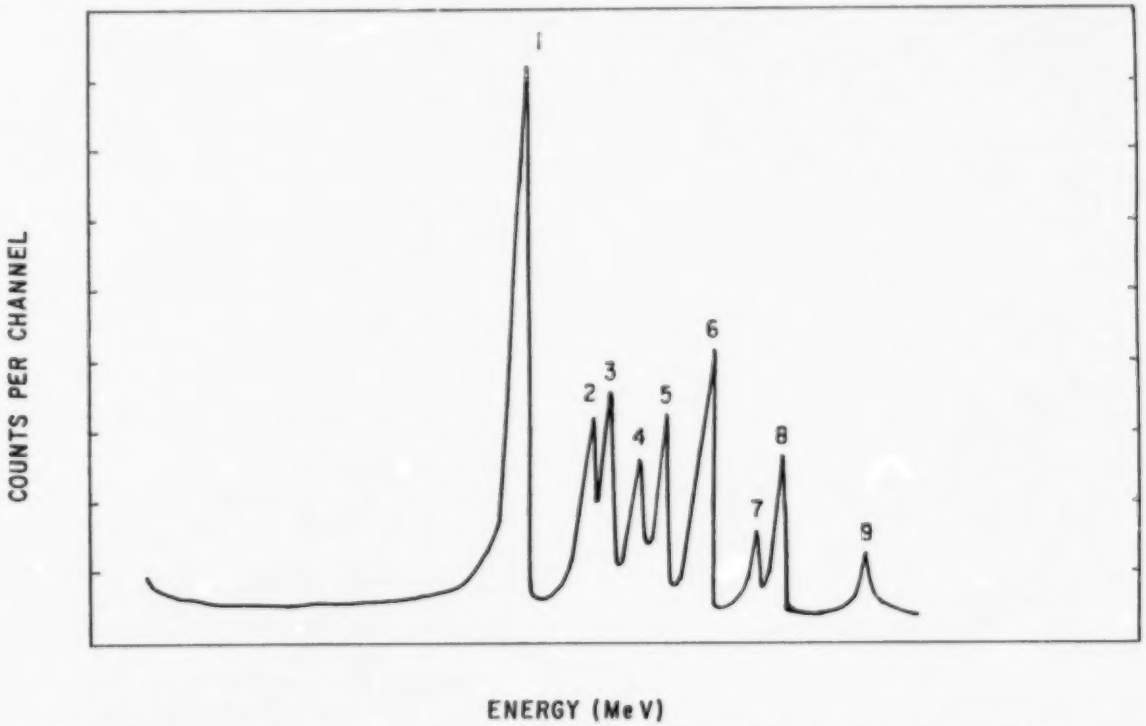

Fig. 3 – Typical alpha spectrum of radium isotopes present in uranium mill tailings taken from Elliot Lake, Ontario. Peak 1, Ra-226; Peak 2, Rn-222; Peak 3, Ra-223 and Ra-224; Peak 4, Bi-212 and Po-218; Peak 5, Rn-220 and Bi-211; Peak 6, Po-216, Rn-219 and Bi-211; Peak 7, Po-215; Peak 8, Po-214; Peak 9, Po-212.

where:

$$\frac{(\sigma Y)^2}{Y^2} = \frac{(\sigma R_t)^2 + (\sigma b_t)^2}{(R_t - b_t)^2} + \frac{(\sigma r_t)^2 + (\sigma b_t)^2}{(r_t - b_t)^2}$$

and:

$$(\sigma y)^2 = y/t_y,$$

where the symbol y represents the appropriate count rate (R, b, r, R_t, b_t or r_t) determined from the counts obtained in the period t_y.

5.1.7 Precision

There are several factors that influence the overall precision of radium-226 activity measurements by alpha spectroscopy. In addition to counting precision, they include sample homogeneity, reproducibility of sample positioning in the alpha spectrometer, precision of weighing and volume measurements, timing errors and instrumental dead time errors. For samples where radium-226 activities are low (less than 100 counts obtained) the counting precision will usually be the largest contributor to the overall precision. For samples whose radium-226 activities are high (greater than 10 000 counts obtained) the contribution of the counting statistics will be negligible. The magnitude of the contribution of procedural uncertainty should be assessed and combined with the counting precision in estimating a reportable overall precision of the measurement (see Appendix A).

Recently four 'standard' uranium tailings samples were submitted to eight Canadian laboratories for radium-226 analysis. The results (204) show that samples analysed using alpha spectroscopy gave average in-laboratory relative standard deviations (RSD) of 5–10% at the 3–10 Bq/g activity level and 2% at the 40 Bq/g activity level. Between-laboratory RSDs were of similar magnitude.

5.2 RADON EMANATION METHOD

5.2.1 Principle

All radium isotopes, together with actinide and lanthanide elements, are separated from the gross sample constituents by coprecipitation with lead sulfate. After dissolving the latter in either alkaline ethylenediaminetetraacetic acid or alkaline diethylenetriaminepentaacetic acid, radium isotopes are then separated from the others by coprecipitation with barium sulfate at pH 4.8. The radium–barium sulfate is redissolved in alkaline EDTA and placed in a bubbler from which the gaseous radon is stripped after a suitable ingrowth period has elapsed. The gas is transferred to a Lucas cell and counted on a scintillation counter.

5.2.2 Interferences

The only possible interference in this method is the presence of radium-224. Its daughter, radon-220, is also an alpha particle emitter, as are its descendents polonium-216, bismuth-212 and polonium-212. These interferences are avoided by allowing sufficient time for radon-220 and its daughters to decay away prior to counting. The presence of radon-222 in the stripping gas would result in a positive error. For this reason, aged compressed gases are used.

5.2.3 Apparatus

- Scintillator detector system: Photomultiplier tube, high-voltage supply, amplifier, timer and scaler
- Vortex mixer
- Syringes: Disposable, 3- or 5-mL capacity
- Micropipettes: 100- and 200-µL and 1.0-mL with disposable tips
- Centrifuge
- Radon bubblers: 25-mL capacity as shown in Figure 4
- Scintillation cells: 100-mL capacity.

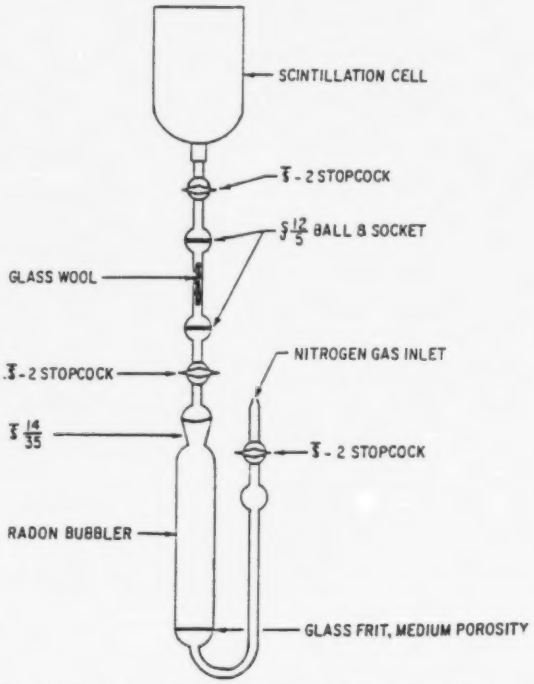

Fig. 4 – Radon emanation apparatus for scintillation cell.

5.2.4 Reagents

- Barium solution (5 mg of Ba per mL): Dissolve 900 mg of $BaCl_2 \cdot 2H_2O$ in 100 mL of deionized water
- Lead nitrate solution (3.2%): Dissolve 32 g of $Pb(NO_3)_2$ in deionized water and dilute to 1 L
- Lead sulfate wash solution: Dissolve 50 g of K_2SO_4 in 1 L of 0.5% H_2SO_4
- Alkaline DTPA (0.2 M): Dissolve 38 g of NaOH in 800 mL of deionized water and add 80 g of diethylenetriaminepentaacetic (DTPA) acid while stirring. Cool, adjust pH to 10.6 with 10 N NaOH and dilute to 1 L with water

- Alkaline DTPA (0.5 M): Dissolve 9.5 g of NaOH in 50 mL of deionized water and add 20 g of DTPA while stirring. Cool, adjust pH to 10.6 with 10 N NaOH and dilute to 100 mL with water
- Sodium hydroxide solution (10 N): Dissolve 400 g NaOH in deionized water and make up to 1 L
- Sulfuric acid (36 N): Reagent grade
- Potassium sulfate: Anhydrous, reagent grade
- Sodium sulfate–acetic acid: Mix 50 mL of 40% Na_2SO_4 solution with 4 mL of glacial acetic acid
- Radium-226 standard solution (4 Bq/mL): Dilute NBS traceable radium-226 in 0.1 N HCl
- Nitrogen gas: Aged for at least 30 d.

5.2.5 Procedures

1. Follow steps 1 to 6 in Section 5.1.5 (Ra-226 alpha spectroscopy method).
2. Disperse the precipitate by injecting 10 mL of a 0.2 M alkaline DTPA solution in the test tube. Mix using a vortex mixer and heat in a hot water bath until the precipitate dissolves. If turbid, add a few drops of 10 N NaOH.
3. Cool in a cold water bath and add 1 mL of the 5 mg/mL barium solution.
4. Using a syringe, rapidly inject 3 mL of the mixed Na_2SO_4/acetic acid into the solution. Allow to cool for 30 min while mixing occasionally.
5. Centrifuge at 2000 rpm for 10 min and decant the supernatant (into a clean test tube if thorium is required).
6. Dissolve the $BaSO_4$ precipitate with 10 mL of 0.2 M alkaline DTPA, as in step 2 above, and transfer the solution to a radon bubbler with the aid of 5 mL of DTPA.
7. Open both the inlet and outlet stopcocks and de-emanate the solution by slowly passing aged nitrogen (2–3 PSI) through the bubbler for about 10 min.
8. Close the inlet and outlet stopcocks, and record time (T_1). Allow 7 d for ingrowth of Rn-222 to reach about 70% of its equilibrium activity. Shorter ingrowth periods can be used with a corresponding reduction in sensitivity.
9. At the end of the ingrowth period, attach an evacuated scintillation cell (less than 100 μ pressure) to the bubbler apparatus. Open the stopcock on the cell and check the assembly for leaks. Slowly open the outlet stopcock on the bubbler and when no further significant bubbling takes place close the stopcock.
10. Adjust the nitrogen gas pressure so that the gas flows at slightly above atmospheric pressure. Connect the hose to the bubbler inlet stopcock and open slowly. When the stopcock can be fully opened without a significant amount of bubbling, the bubbler is at atmospheric pressure.
11. Open the outlet stopcock slowly and allow bubbling to proceed for 10–15 min. Toward the end of the de-emanation, when the bubbling almost ceases, the system is near atmospheric pressure. Close the cell stopcock and record the time (T_2). This is the beginning of Rn-222 decay and ingrowth of its daughters.
12. Store the scintillation cell for at least 5 h to ensure equilibrium between Rn-222 and its daughters and decay of Rn-220 descendants. Count the alpha scintillations from the cell in a scintillation counter.
13. Calibrate each scintillation cell by repeating steps 6 to 12 above, using a solution of Ra-226 with known activity, A_s (Bq). Each scintillation cell should be calibrated periodically to ensure instrument quality control.

5.2.6 Calculations

1. Using the data obtained in step 13 of Section 5.2.5 above, calculate the calibration constant, F, for the instrument and cell from the equation:

$$F = \frac{r'}{A_s (1 - e^{-\lambda t_3}) e^{-\lambda t_4}}$$

where:

r' = net count rate, cpm, for the standard (corrected for the cell background count rate)

A_s = activity of standard Ra-226 in the bubbler (Bq)

t_3 = ingrowth time of Rn-222 in hours

t_4 = decay time of Rn-222 in hours occurring between de-emanation and counting

λ = decay constant of Rn-222, (0.00755 h^{-1}).

2. Using this value of F and the data obtained in steps 8 to 12 of Section 5.2.5 above, calculate the Ra-226 activity concentration, A, in becquerels per litre as follows:

$$A = \frac{R'}{FV} \times \frac{1}{[1 - e^{-\lambda t_4}]} \times \frac{1}{[e^{-\lambda t_b}]} - \frac{\lambda t_c}{[1 - e^{-\lambda t_c}]}$$

where:

- R' = net count rate, cpm, for the sample (corrected for the cell background count rate)
- V = litres of sample used
- t_a = the elapsed time in days between T_1 and T_2 and λ is the decay constant of Rn-222 (0.181 d^{-1}),
- t_b = the time interval in hours between T_2 and T_3 and λ is the decay constant of Rn-222 (0.00755h^{-1})
- t_c = the counting time in minutes and λ is the decay constant of Rn-222 (1.26×10^{-4} min^{-1}).

5.2.7 Precision

Five studies (205) carried out to evaluate the precision of the radon emanation method for radium-226 measurement showed an average relative in-laboratory repeatability of 10% (RSD). The relative between-laboratory reproducibility was found to be between 14% and 18% (RSD).

6. DETERMINATION OF RADIUM-228

6.1 PRINCIPLE

Radium-228 emits beta particles of very low energy (0.05 MeV maximum) which makes its direct measurement impossible using conventional beta-counting systems. Consequently, it is determined indirectly by counting its daughter, actinium-228, a high-energy beta emitter (2.2 MeV maximum). The radium isotopes are first isolated on barium sulfate. Then, after a suitable ingrowth period, actinium-228 is separated from the radium isotopes by coprecipitation with cerous hydroxide (41,59).

6.2 INTERFERENCES

The presence of strontium-90 has been found (206) to give a positive bias to this method.

6.3 APPARATUS

- Beta-counting system: Low-background counting system (see Chapter 3)
- Centrifuge
- Filter holder: Conical, for 25-mm filter with stainless steel support screen
- Membrane filter: PVC or PTFE, 25-mm diameter, 0.2-μ pores
- Centrifuge tubes: Conical, 40-mL capacity
- Plastic discs: 25-mm diameter × 2-mm
- Vortex mixer: Variable speed.

6.4 REAGENTS

- Barium solution (5 mg of Ba per mL): Dissolve 900 mg of $BaCl_2 \cdot 2H_2O$ in 100 mL of deionized water
- Cerium carrier (0.5 mg of Ce per mL): Dissolve 310 mg of $Ce(NO_3)_3 \cdot 6H_2O$ in 200 mL of 0.1 N HNO_3
- Hydrazine dihydrochloride solution (25% w/v): Dissolve 8.25 g of $N_2H_4 \cdot 2HCl$ in deionized water and make up to 25 mL
- Sodium sulfate–acetic acid: Mix 50 mL of 40% Na_2SO_4 solution with 4 mL of glacial acetic acid
- Radium-228 standard solution (4 Bq/mL): Prepare a solution to contain 1 mg of Th per mL by dissolving thorium oxide or nitrate (bottled prior to 1940) using KF/pyrosulfate fusion (see Chapter 2).

6.5 PROCEDURES

1. Follow steps 1 to 5 in Section 5.2.5.
2. With the tip of a disposable syringe directly on top of the $BaSO_4$ precipitate, rapidly inject 5 mL of the sulfate wash solution to disperse the precipitate. Mix using a vortex mixer. Rinse the walls with 2 mL of the sulfate wash.
3. Centrifuge and discard the supernatant.
4. Add 1 mL of deionized water to cover the $BaSO_4$ precipitate. Seal the tube with plastic wrap. Record the time and allow 30 h or more for ingrowth of Ac-228 to greater than 96% of its equilibrium activity.
5. At the end of the ingrowth period, add 5 mL of 0.2 M alkaline DTPA. Mix and heat in a hot-water bath to dissolve the precipitate.
6. Add 1 mL of cerium carrier and mix thoroughly using a vortex mixer.
7. Add 2 drops of 25% hydrazine dihydrochloride and 2.5 mL of 10 N NaOH. Mix thoroughly and heat in a hot-water bath for 10 min.
8. Cool in a cold-water bath for 5 min. Filter the precipitate of cerous hydroxide onto a 25-mm, 0.2-μ membrane filter. Rinse twice with 5-mL aliquots of 50% ethanol.
9. Glue the filter onto a 25-mm plastic disc. Dry under a heat lamp and cover with aluminum foil for the beta counting of Ac-228.

   Note: The separation of Ac-228 by coprecipitation with cerous hydroxide (steps 7–9 above) takes approximately 30 min and in view of the short half life of Ac-228 (6.13 h), the authors recommend samples be prepared one at a time just before beta counting.
10. Place the sample source in the beta counter and record the total beta counts obtained in a suitable period of time. Calculate the count rate, R.
11. Prepare a calibration source by placing an exact activity (in Bq), A_s, of the standard Ra-228 solution into a conical centrifuge tube and perform steps 1 to 9 above.
12. Count the radium (actually Ac-228) calibration source in the beta counter for a suitable period of time. Calculate the count rate, r.
13. Prepare a blank source in the same manner as the calibration source.
14. Count the blank source in the beta counter under the same conditions used for the calibration source. Record the count rate, b.

6.6 CALCULATIONS

1. Calculate the calibration constant, F, from the equation:

$$F = \frac{r - b}{A_s} \times e^{0.113\Delta t}$$

where:

Δt is the elapsed time (in hours) between the time of precipitation with $Ce(OH)_3$ and the time of counting.

2. Calculate the Ra-228 content of the sample, A (Bq/g) from the equation:

$$A = \frac{R - b}{FW} \times e^{0.113\Delta t}$$

where:

W is the weight (in grams) of the solid sample originally taken for sample decomposition. In the case of a liquid sample, W may represent volume (in litres) and the results are expressed in units of Bq/L.

3. Calculate the radiometric counting precision, σA, of the Ra-228 measurement according to the equation:

$$\sigma A = A \times \left[\frac{(\sigma R)^2 + (\sigma b)^2}{(R - b)^2} + \frac{(\sigma r)^2 + (\sigma b)^2}{(r - b)^2} \right]^{0.5}$$

where:

$$(\sigma y)^2 = y/t_y$$

where the symbol y represents the appropriate count rate (R, r or b) determined from counts measured in the period t_y.

6.7 PRECISION

There are several factors that influence the overall precision of radium-228 activity measurements by beta spectrometry. They include counting precision, sample homogeneity, reproducibility of sample positioning in the beta spectrometer, precision of weighing and volume measurements, timing errors and instrumental dead-time errors. For samples where radium-228 activites are low (less than 100 counts obtained) the counting precision will usually be the largest contributor to the overall precision. For samples whose radium-228 activities are high (greater than 10 000 counts obtained) the contribution of the counting statistics will be negligible. The magnitude of the contribution of procedural uncertainty should be assessed and combined with the counting precision in estimating a reportable overall precision of the measurement (see Appendix).

In a recent interlaboratory study (204) carried out by several Canadian laboratories using uranium mill tailings, the relative repeatability (average in-laboratory RSD) of this method was found to be 10% at the 1 Bq/g level. In cases where the activity of radium-228 is low, the main source of uncertainty may be from the counting statistics.

7. DETERMINATION OF LEAD-210

7.1 PRINCIPLE

Lead-210 is determined indirectly by measuring the beta activity of its daughter bismuth-210. Bismuth-210 is allowed to grow in for a minimum of 30 d to achieve an equilibrium of greater than 98%. It is then separated from lead-210 by solvent extraction using a 0.1% solution of diethylammonium diethyldithiocarbamate in chloroform. Subsequently, bismuth-210 is precipitated as bismuth oxychloride, BiOCl. After allowing five or more hours for other short-lived bismuth isotopes to decay, bismuth-210 is determined using a beta counter (91). Its chemical recovery is determined by measuring the activity of the isotopic tracer, bismuth-207 (59).

7.2 INTERFERENCES

The interference of bismuth-212 (60 min half-life) from the thorium-232 decay series can be avoided by allowing at least five hours between precipitation and counting of the sample.

7.3 APPARATUS

- Low-background beta-counting system (see Chapter 3)
- Gamma-counting system: NaI crystal, power supply, multichannel analyzer
- Magnetic stirrer: Six-place with single-speed controller
- Hotplate: Variable temperature, Teflon-coated 40-cm × 80-cm surface
- Vortex mixer: Variable speed
- Filter holder: Conical with stainless steel support screen for 25-mm filter
- Membrane filter: Cellulose acetate 25-mm diameter, 0.45-μ pores
- Pipettes: Disposable polyethylene, 4-mL capacity
- Plastic discs: 25-mm diameter × 2-mm.

7.4 REAGENTS

- DDTC solution (0.1%): Dissolve 1.0 g of diethylammonium diethyldithiocarbamate in 1 L chloroform; prepare daily
- Bismuth carrier (5 mg per mL): Dissolve 5.80 g of $Bi(NO_3)_2 \cdot 5H_2O$ in 2 N HCl and dilute to 500 mL
- Ascorbic acid: Reagent grade
- Nitric acid (16 N): Reagent grade
- Ammonium hydroxide (7 N): Reagent grade
- Lead-210 standard solution (4 Bq/mL): Dilute NBS traceable lead-210 in 0.1 N HCl.

7.5 PROCEDURES

1. Place a Teflon-coated stirrer in the 2 N HCl sample solution prepared in Procedures B, E or F of Chapter 2 (Sections 2.5.2, 2.5.5 and 2.5.6, respectively).
2. Add enough ascorbic acid to reduce any ferric iron present and 500 mg in excess.
3. Add 10 mL of 0.1% DDTC in chloroform to the 100-mL sample solution (or 20 mL to a 500-mL sample solution). Cover with a watch glass.

   WARNING: The handling and evaporation of chloroform (steps 3–8) should be conducted in a well-ventilated fumehood.
4. Stir vigorously with magnetic stirrer for 1 min. Record the time as the beginning of Bi-210 decay.

   Note: Preset stirrer speed to give thorough mixing of the two phases.
5. Allow 3–5 min for phase separation and, using a disposable polyethlene pipette, transfer the DDTC extract to a 100-mL beaker.
6. Repeat the DDTC extraction two more times and add extracts to the beaker. The last extract should be colourless. If not, repeat extraction until the extract is clear.

   Note: Using one six-place magnetic stirrer, 6 samples can be extracted in less than 80 min, and if two six-place stirrers are used, 12 samples can be extracted in less than 2 h.
7. Evaporate the combined extract to dryness on a hotplate set at 60–65°C.
8. Add 5 mL of 16 N HNO_3, cover with watch glass and digest until clear. Remove watch glass and evaporate to a volume of 2 mL. Cool to room temperature.
9. Rinse the walls with 2–3 mL of deionized water, swirl to mix and transfer to a 40-mL centrifuge tube with the aid of up to 5 mL of water.
10. Add 1.0 mL of bismuth carrier. While mixing with a vortex mixer, add 7 N NH_4OH until the solution just turns cloudy (pH should be 8).
11. Heat in a hot-water bath for 15 min and mix contents by vortex mixer every 3–4 min.
12. Remove and cool in a cold-water bath.
13. Centrifuge, decant supernate, and invert centrifuge tube on a clean tissue to drain.
14. Rinse the walls with 1 mL of hot 3 N HCl and mix with a vortex mixer to dissolve the precipitate.
15. Add 30–35 mL of deionized water. A fine, silky white suspension of BiOCl appears. Heat in hot-water bath at 80°C.

    Note: If the HNO_3 oxidation in step 8 above is incomplete, the BiOCl precipitate appears very coarse and yellowish.
16. Filter the BiOCl onto a 0.45-μ membrane filter. Wash twice with 5-mL portions of hot water.

17. Glue filter onto a plastic disc, dry under infrared heat lamp and cover with aluminum foil. Allow 10 h for other short-lived bismuth isotopes, such as Bi-211, Bi-212 and Bi-214, to decay.
18. Place the sample source in the beta counter and determine the Bi-210 count rate, R. Compute the elapsed time from the first DDTC extraction to the mid-point of the measurement, t (in hours).
19. Place the sample source in the gamma spectrometer and determine the Bi-207 count rate, R_t (see Chapter 4).
20. Prepare a calibration source by taking aliquots of standard Pb-210 and Bi-207 and proceeding through steps 2–17 above. Use the same aliquot of Bi-207 as employed for the sample at the decomposition stage (see Chapter 2).
21. Place the calibration source in the beta counter and determine the Bi-210 count rate, r. Compute the elapsed time from the first DDTC extraction to the mid-point of the measurement, t_2 (in hours).
22. Place the calibration source in the gamma spectrometer and determine the Bi-207 count rate, r_t (see Chapter 4).
23. Prepare a blank reagent source in the same manner as the calibration source.
24. Determine the Bi-210 beta count rate, b, and the Bi-207 gamma count rate, b_t, for the blank source (see Chapter 4).

7.6 CALCULATIONS

1. Calculate the apparent calibration constant, F, from the equation:

$$F = \frac{r - b}{A_s} \times e^{0.00576t_2}$$

where A_s is the activity of standard Pb-210 aliquot and t_2 is the elapsed time, in hours, between the first DDTC extraction and the mid-point of the beta measurement.

2. Calculate the chemical yield of the sample source relative to that of the calibration source from the equation:

$$Y = \frac{R_t - b_t}{r_t - b_t}$$

3. Calculate the Pb-210 activity of the sample, A (Bq/g), according to the equation:

$$A = \frac{R - b}{Y F W} \times e^{0.00576t}$$

where:

W is the weight (in grams) of the solid sample originally taken and t is the elapsed time in hours between the first DDTC extraction and the mid-point of the beta measurement. In the case of liquid samples, W will represent volume.

4. Calculate the radiometric counting precision, σA, of the Pb-210 measurement according to the equation:

$$\sigma A = A \times \left[\frac{(\sigma R)^2 + (\sigma b)^2}{(R - b)^2} + \frac{(\sigma r)^2 + (\sigma b)^2}{(r - b)^2} + \frac{(\sigma Y)^2}{Y^2} \right]^{0.5}$$

where:

$$\frac{(\sigma Y)^2}{Y^2} = \frac{(\sigma R_t)^2 + (\sigma b_t)^2}{(R_t - b_t)^2} + \frac{(\sigma r_t)^2 + (\sigma b_t)^2}{(r_t - b_t)^2}$$

and:

$$(\sigma y)^2 = y/t_y$$

where the symbol y represents the appropriate count rate (R, b, r, R_t, b_t or r_t) determined from the counts obtained in the period t_y.

7.7 PRECISION

There are several factors that influence the overall precision of lead-210 activity measurements. In addition to counting precision, they include sample homogeneity, reproducibility of sample positioning in the beta spectrometer, precision of weighing and volume measurements, timing errors and instrumental dead time errors. For samples in which lead-210 activities are low (less than 100 counts obtained), the counting precision will usually be the largest contributor to the overall precision. For samples in which lead-210 activities are high (greater than 10 000 counts obtained) the contribution of the counting statistics will be negligible. The magnitude of the contribution of procedural uncertainty should be assessed and combined with the counting precision in estimating a reportable overall precision of the measurement (see Appendix).

Recently, four 'standard' uranium mill tailings samples were submitted to eight Canadian laboratories for lead-210 analysis. The results (204) show that samples analysed using the method described here gave average relative laboratory repeatabilities of 5–10% (RSD) at the 3–10 Bq/g activity levels and 2% at the 40 Bq/g activity level. The reproducibilities among the participating laboratories (RSDs of the laboratory mean values) were of the same order as the repeatabilities.

8. DETERMINATION OF TOTAL THORIUM BY SPECTROPHOTOMETRY

8.1 PRINCIPLE

Many cations react with arsenazo III (1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis(azo-2-phenylarsonic acid)) to form stable coloured complexes (135–137). The high stability of these complexes permits the spectrophotometric determination of the cations in strong acid media and in the presence of complex-forming anions such as phosphate, sulfate, fluoride, ethylenediaminetetraacetate and others (135–137,207,208).

Thorium, together with other multivalent elements with ionic radii larger than 1.0 atomic units in solution, is separated from other cations by coprecipitation with lead sulfate. The lead sulfate is dissolved in diethylenetriaminepentaacetate solution after which thorium is extracted into bis(2-ethylhexyl)phosphoric acid. Finally, thorium is back extracted into an aqueous solution of oxalic acid for spectrophotometric determination with arsenazo III (59).

The thorium–arsenazo III complex is developed in a 3 N HCL medium. The wavelength of the maximum absorbance is at 665 nm.

8.2 INTERFERENCES

There are no interferences.

8.3 APPARATUS

- Spectrophotometer: With 10-mm and 50-mm absorption cells
- Automatic shaker: Reciprocating with variable speed
- Vortex mixer: Variable speed
- Bottles: Polypropylene with screw cap, 100-mL
- Volumetric test tubes: Calibrated at 25-mL and 50-mL
- Culture tubes: Disposable, 150-mm × 20-mm
- Pipettes: Glass Pasteur and polypropylene disposable.

8.4 REAGENTS

- Thorium standard solution (100 mg/L): Dissolve 207 mg $Th(NO_3)_4$ in 0.1 N HCl and dilute to 1 L
- HDEHP (5% v/v prewashed): Dilute 50 mL of bis-(2-ethylhexyl)phosphoric acid to 950 mL with n-heptane. Wash twice, for one minute each with 200-mL portions of a one-to-one mixture of diammonium citrate and concentrated ammonium hydroxide and twice with 200-mL portions of 4 M HNO_3. Just before use, wash with a one-half-volume portion of 4 M HNO_3 for one minute (6)
- Aluminum nitrate (2 M): Dissolve 750 g of $Al(NO_3)_3 \cdot 9H_2O$ in 450 mL of deionized water and 50 mL of 16 N HNO_3 with heating. Under vacuum, filter the solution through two glass-fibre filters. Dilute to 1 L
- Hydrogen peroxide (30%): Reagent grade
- Oxalic acid solution (0.4 M): Dissolve 36 g of oxalic acid in deionized water and dilute to 1 L
- Arsenazo III (0.1%): Dissolve 1 g of Arsenazo III in 1 L of deionized water
- Toluene: Reagent grade
- Nitric acid (16 N): Reagent grade.

8.5 PROCEDURES

1. Transfer the DTPA–$PbSO_4$ solution (follow steps 1–8 of Section 5.1.5) or the DTPA–acetic acid solution after the removal of $BaSO_4$ (step 11 of Section 5.1.5) into a 100-mL polypropylene bottle, and dilute to 25 mL with deionized water.
2. Add 10 mL of 16 N HNO_3, 5 mL of 2 M $Al(NO_3)_3$ and 1 mL of 30% H_2O_2, tighten the cap, shake vigorously for 20 s, loosen the cap and allow to stand for 10 min.
3. Add 10 mL of the prewashed 5% HDEHP to the mixture, tighten the cap, place the bottle horizontally in an automatic reciprocating shaker and shake vigorously (end-to-end) for 15 min.
4. Open the cap carefully to release pressure, empty contents into a 150-mm × 20-mm test tube and allow 10 min for phase separation.
5. Siphon off the lower aqueous layer using a glass Pasteur pipette connected to an aspirator.

   Note: The pipette should be connected by rubber tubing to a safety flask, which in turn is connected to the aspirator. By bending the rubber tubing an inch from the top of the pipette and controlling pressure exerted on the bend, one can regulate or stop the flow of the siphoning action. This phase separation is much cleaner and easier to perform than using a separatory funnel. This is particularly beneficial when small volumes are involved as in the following steps.
6. Add 10 mL of 4 N HNO_3 and 0.5 mL of 30% H_2O_2 to the organic phase. Mix vigorously using a vortex mixer for 30 s and allow 5 min for phase separation. Siphon off the aqueous layer and discard.
7. Repeat step 6 with 10 mL of 4 N HNO_3 only.
8. Add 10 mL of toluene and 6 mL of 0.4 M oxalic acid to the organic phase. Mix vigorously using a vortex mixer for 2 min. Allow 5 min for phase separation.

   Note: If a fine, white precipitate appears, it indicates the presence of at least 1.5 mg of Th-232 in the sample aliquot. Reduce the sample size by a factor of at least 20,

or dilute the DTPA–$PbSO_4$ and take an aliquot.

9. Using a disposable pipette, remove the lower oxalic acid extract and place it in a 25-mL volumetric test tube.
10. Repeat extraction with 6 mL of 0.4 M oxalic acid and combine the extracts.
11. Add 6 mL of 12 N HCl and 0.5 mL of the 0.1% Arsenazo III solution to the oxalic acid extract and dilute to 25 mL with deionized water.
12. In a spectrophotometer, determine the absorbance at 665 nm after adjusting to zero absorbance using a reagent blank.
13. Carry standard thorium solutions, containing 1–25 μg, through the entire procedure and plot absorbance versus micrograms thorium. The amount of total thorium in a sample aliquot can either be read directly from this plot or calculated from the regression equation for the calibration curve.

8.6 CALCULATIONS

The quantity of thorium in the sample can be calculated from the equation:

$$Th, = \frac{R_u - R_b}{R_s - R_b} \times Q_s$$

where:

R_b = mean absorbance reading of reagent blank

R_s = mean absorbance reading of standard

R_u = mean absorbance reading of sample

Q_s = thorium in standard sample, μg.

The thorium in the original sample, expressed in μg/g or μg/mL, can be calculated when the appropriate dilution, concentration and extraction factors are used.

8.7 PRECISION

The precision is ±5%. The detection limit is 0.05 μg.

9. DETERMINATION OF THORIUM ISOTOPES BY ALPHA SPECTROSCOPY

9.1 PRINCIPLE

The naturally occurring, alpha-emitting thorium isotopes (thorium-227, thorium-228, thorium-230 and thorium-232) are normally determined by alpha spectroscopy. If thorium-227 is to be measured in the presence of thorium-228 or thorium-230, the alpha spectrum must be recorded immediately after preparation of the source. Otherwise, the ingrowth of the daughters of thorium-228 will directly interfere with the thorium-227 peak. The thorium isotopes are first isolated by chemical separations and then they are coprecipitated with 50 μg of cerium carrier from a strongly alkaline EDTA solution. The precipitate is filtered onto an alkali-resistant membrane filter to provide the source for alpha spectroscopy (59,60). Under certain conditions the observed resolution approaches that obtained by electrodeposition on a polished stainless steel disc (35).

The chemical recovery is determined by the use of the thorium-234 tracer which is added at the time of sample dissolution (see Chapter 2). Apparent recoveries greater than 100% can occur if the sample contains a large amount of uranium-238, the parent of thorium-234 (24 d half-life).

9.2 INTERFERENCES

This method involves isolation of thorium isotopes from all other elements. Therefore, the only interferences are spectral. When the alpha source is kept thin, high-resolution spectra are assured and no interferences should be encountered. The source thickness will increase as the amount of thorium-232 increases above 50 μg. Thick sources will result in poor resolution and self-absorption. A correction for these effects can be made by means of a computer simulation (196).

9.3 APPARATUS

- Alpha spectrometer: Surface barrier or silicon-diffused junction detector, preamplifier, bias voltage supply, linear amplifier, multichannel analyzer
- Beta counter: Low-background beta-counting system (see Chapter 3)
- Filter holder: Conical with stainless steel support screen for 25-mm filter
- Membrane filters: PVC or PTFE, 25-mm diameter, 0.1-μ porosity
- Vortex mixer: Variable speed
- Plastic discs: 25-mm diameter × 2-mm.

9.4 REAGENTS

- Thorium-228 standard solution (4 Bq/mL): Dilute NBS traceable thorium-228 in 0.1 N HCl
- Alkaline EDTA (0.05 M): Dissolve 9.31 g of disodium ethylenediaminetetraacetic acid dihydrate in 400 mL of deionized water and 4.5 mL of 10 N NaOH. Adjust the pH to 10.6 with 10 N NaOH and dilute the solution to 500 mL
- Cerium carrier solution (0.5 mg of Ce per mL): Dissolve 310 mg of $Ce(NO_3)_3 \cdot 6H_2O$ in 200 mL of 0.1 N HNO_3. Following steps 5 to 13 below, prepare a blank cerium hydroxide source. Determine the alpha particle spectrum. If thorium-232 and its daughters are present, purify the carrier according to the published procedure (6,209).

9.5 PROCEDURES

1. Follow steps 1 to 10 of the procedure for the determination of total thorium by spectrophotometry, (Section 8.5) with one exception, i.e., place the oxalic acid extracts in a 50-mL beaker.
2. Add 5 mL of 15 N HNO_3 and 2 mL of 70% $HClO_4$, cover with a watch glass and digest at 100°C until clear.
3. Remove the watch glass and evaporate just to dryness. Cool the beaker and its contents.
4. Use heat and agitation to dissolve the residue in 5 mL of 1N HCl. Cool.
5. Transfer to a 40-mL centrifuge tube, rinse the beaker with 6 mL of 0.05 M EDTA and add to the centrifuge tube.
6. Add 100 μL of the cerium carrier solution and mix thoroughly using a vortex mixer.
7. Add 2 drops of 25% hydrazine dihydrochloride and 2.5 mL of 10 N NaOH. Mix thoroughly using a vortex mixer and heat in a hot-water bath for 10 min. A milky opalescence, barely visible, will be observed.
8. Cool in a cold water bath for 10 min.
9. Prepare a 25-mm diameter, 0.1-μ membrane filter on a filter holder with a stainless steel support screen.
10. Mix the contents of the centrifuge tube vigorously using a vortex mixer, and pour into the filter holder.
11. Rinse 5 mL of 1 N NaOH around the sides of the centrifuge tube. Mix and add to the filter holder after the sample has passed through.
12. Wash the centrifuge tube, filter holder and precipitate with three 5-mL portions of 80% ethanol.
13. Remove the filter carefully. Glue it to a plastic disc and dry under an infrared heat lamp at a distance of 10 cm.

14. Place the sample source in the alpha spectrometer and record the alpha particle spectrum on the multichannel analyzer. Depending on the source thickness, the activities of the thorium isotopes present and the age of the source, the spectrum should be similar to that shown in Figure 5. This is a typical alpha particle spectrum of thorium isotopes for Elliot Lake uranium mill tailings.
15. After a suitable counting time, record the total counts collected under the Th-232, Th-230 and Th-228 peaks. Calculate their respective count rates, counts per minute, R_2, R_0, and R_8.
16. Determine the beta count rate, R_t, for the Th-234 contained in the sample source.
17. Prepare a calibration source by placing an exact aliquot of the standard Th-228 solution, A_s, and an aliquot of the standard Th-234 solution, identical to that employed with samples at the decomposition stage (see Chapter 2), in a centrifuge tube. Follow the radiochemical procedure steps 1–13 above.
18. Place the calibration source in the alpha spectrometer and, under the same conditions used for the sample source, record the count rate, r, for the Th-228 peak.
19. Determine the Th-234 beta count rate of the calibration source, r_t.
20. Prepare a blank source for background determination by repeating steps 1 to 13 above using reagents only.
21. Place the blank source in the alpha spectrometer and, under the same conditions used for the sample source, record the background count rates, b_2, b_0 and b_8 for Th-232, Th-230 and Th-228, respectively.
22. Determine the background Th-234 beta count rate, b_t, using the blank source.

9.6 CALCULATIONS

1. Calculate the apparent calibration constant, F, from the equation:

$$F = \frac{r - b_8}{A_s}.$$

2. Calculate the chemical yield, Y, of the sample source relative to that of the calibration source from the equation:

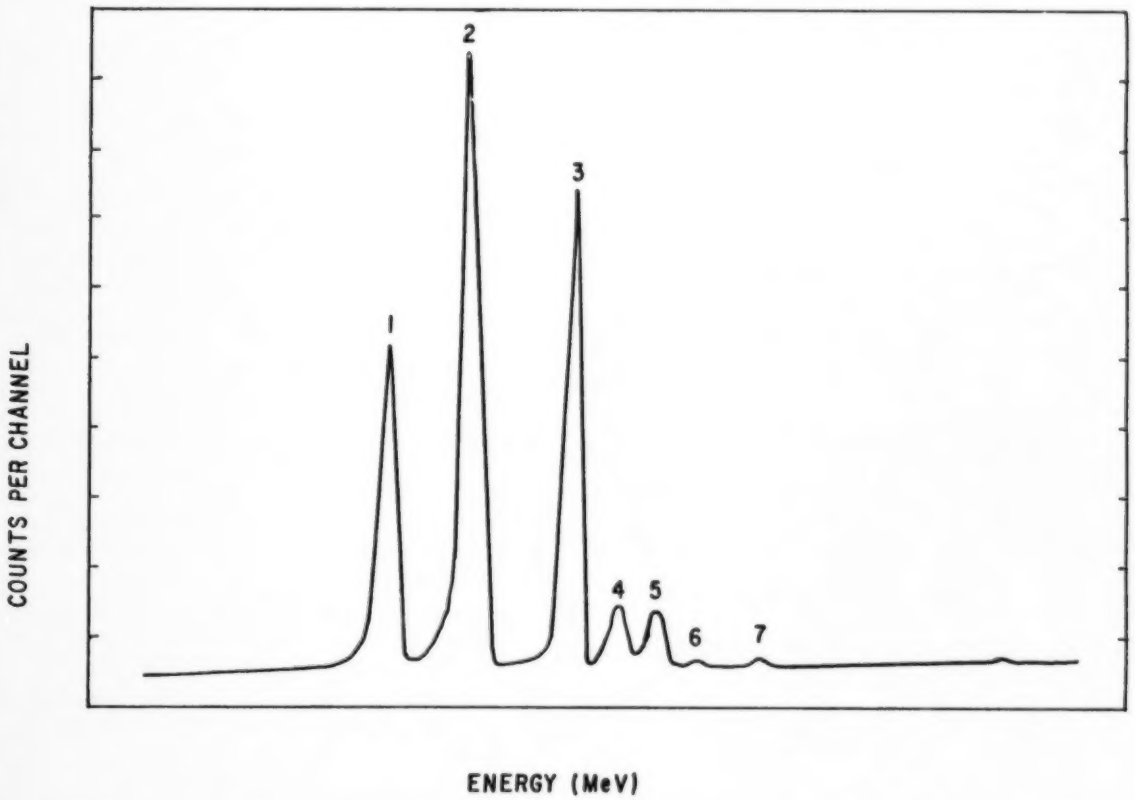

Fig. 5 – Typical alpha spectrum of thorium isotopes present in uranium mill tailings taken from Elliot Lake, Ontario. Peak 1, Th-232; Peak 2, Th-230; Peak 3, Th-228; Peak 4, Ra-224; Peak 5, Th-227; Peak 6, Rn-220; Peak 7, Po-216.

$$Y = \frac{R_t - b_t}{r_t - b_t}.$$

3. Calculate the Th-232, Th-230 and Th-228 activities, A_2, A_0 and A_8 (Bq/g), of the sample according to the equations:

$$A_2 = \frac{R_2 - b_2}{FWY}$$

$$A_0 = \frac{R_0 - b_0}{FWY}$$

$$A_8 = \frac{R_8 - b_8}{FWY}$$

where:

W is the weight in grams of solid sample originally taken. In the case of liquid samples, W will represent volume (litres).

4. Calculate the radiometric counting precisions, σA_i ($i = 2,0,8$), of the thorium isotope measurements according to the equation:

$$\sigma A_i = A_i \times \left[\frac{(\sigma R_i)^2 + (\sigma b_i)^2}{(R_i - b_i)^2} + \frac{(\sigma r)^2 + (\sigma b_8)^2}{(r - b_8)^2} + \frac{(\sigma Y)^2}{Y^2} \right]^{0.5}$$

where:

$$\frac{(\sigma Y)^2}{Y^2} = \frac{(\sigma R_t)^2 + (\sigma b_t)^2}{(R_t - b_t)^2} + \frac{(\sigma r_t)^2 + (\sigma b_t)^2}{(r_t - b_t)^2}$$

and:

$$(\sigma y)^2 = y/t_y$$

where the symbol y represents the appropriate count rate (R_i, b_i, r, b_8, R_t, b_t or r_t), determined from counts measured in the period t_y.

9.7 PRECISION

There are several factors that influence the overall precision of thorium isotope activity measurements by alpha spectroscopy. In addition to counting precision, they include sample homogeneity, reproducibility of sample positioning in the alpha spectrometer, precision of weighing and volume measurements, timing errors and instrumental dead-time errors. For samples where the individual thorium isotope activity is low (less than 100 counts obtained), the counting precision will usually be the largest contributor to the overall precision. For samples where the individual thorium isotope activity is high (greater than 10 000 counts obtained), the contribution of the counting statistics will be negligible. The magnitude of the contribution of procedural uncertainty should be assessed and combined with the counting precision in estimating a reportable overall precision of the measurement (see Appendix A).

Recently four 'standard' uranium mill tailings samples were submitted to eight Canadian laboratories for thorium isotope analysis. The results (204) show that samples analysed using alpha spectroscopy gave average relative in-laboratory repeatabilities of 6–10% (RSD) at the 0.2–10 Bq/g activity level and 1% at the 40 Bq/g activity levels. The reproducibilities (between-laboratory RSDs) among all the participating laboratories were of the same magnitude.

10. DETERMINATION OF RADON-222

10.1 PRINCIPLE

There are many suitable techniques available for determining radon-222 in the atmosphere (104–128). For the purposes of this manual, time integration has been chosen as the most appropriate because of its low cost and relative simplicity (119). The method involves atmospheric sampling over 48 h and simultaneous collection in commercially-available radon-tight Mylar bags, transfer of the radon to cooled charcoal and finally gamma-counting of the radon daughters after secular equilibrium has been attained. The activity so determined is related to the atmospheric radon-222 content over the 48-h sampling period. A maximum error of ±15% due to averaging can be expected.

10.2 INTERFERENCES

No radioactive elements or isotopes.

10.3 APPARATUS

- Aquarium pump: Flowrate of approximately 3 L/min equipped with a needle valve capable of restricting the flow from 0 to 125 mL/min
- Lead storage battery: 12 volt; 70 amp hour capacity
- Power inverter
- Mylar sample bags: 40-L capacity (radon tight)
- Small funnel
- Rubber tubing: 2 m of 3-mm ID
- Air filter: Cellulose acetate membrane filter
- Graduated cylinder: 10-mL
- NaI gamma detector (lead shielded)
- Multichannel analyzer
- Detector power supply
- Granulated charcoal
- MnO_2 impregnated acrylic fibre
- Dry ice/acetone bath
- Freeze-out trap containing copper filaments
- Drying column
- Anhydrous calcium chloride
- Aged air
- Drying tube.

10.4 REAGENTS

Radium-226 solution: NBS standard.

10.5 (A) PROCEDURES FOR SYSTEM CALIBRATION

1. Set up the apparatus as shown in Figure 6 and adjust the needle valve to deliver a flowrate, G, of approximately 10 mL/min. Calibrate the flowrate by displacing water from an inverted graduated cylinder for a measured period of time. Repeat several times. See Note 1.
2. Prepare a standard Rn-222 calibration tube by adsorbing a known activity, approximately 2000 Bq (60 nCi), of Ra-226 onto acrylic fibre impregnated with manganese dioxide. This material is known to hold radium strongly but to emanate radon freely (21–24). Dry the fibre containing the radium in an oven at 110°C and carefully place it into a drying tube. Prior to starting the calibration measurements it is imperative that old ingrown radon be removed from the calibration tube. See Note 2.
3. Remove sampling funnel and connect the calibration tube to the sample line.
4. Connect the aged air to the calibration tube and start the calibrated pump. Record the time and date as T_1. Pass aged air through the calibration tube for exactly t min at 10 mL/min and record the time and date of $T_1 + t$ as T_2. Disconnect the calibration tube from the sample line and sample aged-air only for approximately 48 h.
5. After 48 h of sampling time stop the pump and record the time and date as T_3. See Note 3.
6. As soon as practical, transfer the gas from the Mylar collection bag, by using the aquarium pump, to the charcoal trap cooled to –76°C in a dry ice/acetone bath. The needle valve should be adjusted to provide a flowrate of 200 mL/min for this operation, which should take approximately 20 min. See Note 4.
7. Remove the charcoal from the trap and transfer to a suitable sealed container for the gamma-ray measurement. Add fresh charcoal to the trap.
8. Allow 3 h for radioactive equilibrium to be achieved between the radon and its daughters. Place the charcoal in the counting position on the lead-shielded gamma-ray detector. Set the multichannel analyzer to accept energies from 0.15 to 1.5 MeV which will include the peaks of interest from Pb-214 at 0.295 MeV and 0.352 MeV and from Bi-214 at 0.609 MeV.
9. Count the charcoal for 2 h, recording the start date and time as T_4. Express the result in counts per minute r.
10. Repeat steps 4 to 9 but using only aged air as the sample to obtain a system blank, b.
11. Correct for the Rn-222 that has decayed from T_2 to T_4 and for the background contribution by the equation:

$$r^{corr} = (r - b)\, e^{0.181\Delta t}$$

where:

Δt is the elapsed time, in days, from the time of sampling to the time of analysis ($T_4 - T_2$).

12. Calculate the total activity, A_s, in Bq, collected in the Mylar bag by using the equation

$$A_s = A_{Ra}\,(1 - e^{-kt})$$

where A_{Ra} is the activity of Ra-226 adsorbed into the acrylic fibre, k is the Rn-222 decay constant and is equal to 1.25×10^{-4} min^{-1} and t is $T_2 - T_1$, expressed in minutes.

For example, if 2444 Bq of standard Ra-226 is adsorbed onto the acrylic fibre/manganese dioxide medium and aged air is passed through it for 3 min, the total activity of Rn-222 collected in the collection bag will be

$$2444\ (1 - e^{-3 \times 1.25 \times 10^{-4}}) = 0.91\ Bq.$$

13. Repeat calibration steps 3 to 11 three more times for 2t, 3t and 4t min.
14. Prepare a table relating the activity of Rn-222 as collected to the corrected count rate r^{corr}.
15. Determine the average calibration factor, F, and its precision by linear regression analysis. Note that F (count rate/unit of activity) refer to activity in the sampling bag at the end of the collection period.

(B) PROCEDURES FOR ATMOSPHERIC SAMPLE COLLECTION AND MEASUREMENT

16. For sampling of the atmosphere use the apparatus shown in Figure 6 and described in step 1 above.
17. Locate the sample tube at the desired sampling point, taking care to ensure that the pump, battery and sample bags are protected from the weather.
18. Commence atmospheric sampling at the calibrated flowrate, G (10 mL/min), recording the date and time as T_5.
19. After approximately 48 h, stop sampling and record the date and times as T_6.

    Return the collection bag to the laboratory and as soon as possible transfer the gas to the charcoal as described in step 6 above. Remove the charcoal from the trap, transfer to a suitable sealed container, allow 3 h for daughter ingrowth and commence counting as described in steps 8 and 9. Record the start of the count time as T_7. See Note 3.

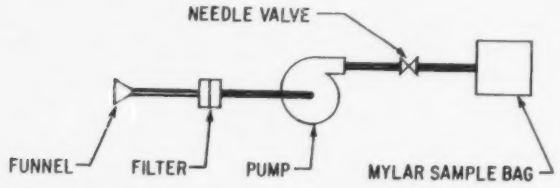

Fig. 6 – Schematic of apparatus for integrated radon sampling.

10.6 CALCULATIONS

1. Correct the observed count rate, R, for decay and background contribution by

$$R^{corr} = (R - b)\ e^{0.181\Delta t}$$

where:

Δt = elapsed time, in days, from the time of sampling to the time of analysis ($T_7 - T_6$).

2. Calculate the atmospheric Rn-222 content, A, in (Bq/L), by the equation

$$A = \frac{k\ R^{corr}}{FG\ (1 - e^{-.181\Delta t_2})}$$

where:

k = 0.125 (Rn decay constant in $min^{-1} \times 1000$)
F = the calibration constant in units of gamma count rate/Bq
G = the calibrated flowrate in mL/min
Δt_2 = the sampling period expressed in days ($T_6 - T_5$).

10.7 PRECISION

Measurement precision is affected by the sampling reproducibility and counting statistics, particularly for low radon-activity samples. The calibration, the sampling procedures, and a measurement precision estimate can be derived from the statistics of the regression fit to the data. Additionally, since the atmospheric radon concentration can be dynamic, reproducibility of the measurement can be affected by activity variations during the sampling period. The decay correction assumes that the sampling rate is constant but the results represent concentration variations during sampling. In the most extreme cases of variations, the error incurred by the approximation is likely to be less than 15% (119).

NOTES

1. To prevent rain from being drawn into the sampling tube and subsequent saturation of the cellulose acetate filter, a funnel may be attached to the sampling tube.
2. It is necessary to flush out ingrown radon from the calibration tube immediately prior to starting step 3. This can be accomplished by passing aged air through the tube at a flowrate of 200 mL/min for 10 min.
3. During atmospheric sampling in the field, this step would be the last field step prior to returning the sample to the laboratory. For calibration purposes, however, it is assumed that most of the measurements will be done in the laboratory.
4. It may be advisable to use the ice-water cooled freeze-out trap and the calcium chloride drying tube in the transfer line if atmospheric sampling took place during humid conditions to prevent water saturation of the charcoal. The trap and drying tube are placed between the Mylar bag and the charcoal trap. However, the use of these two dessicating devices must be checked with the standard to ensure that radon removal does not take place in the system prior to the charcoal trap.

11. DETERMINATION OF RADON-222, RADON-220 AND RADON-219

11.1 PRINCIPLE

This method is based on a publication of Perdue et al. (128) describing the simultaneous measurement of the three radon isotopes (radon-222, radon-220 and radon-219) using an alpha spectrometric technique. It is a modification of the two-filter Lucas cell method described by Thomas and Le Clare (210). As air flows through the system the first filter passes the radon isotopes but traps their daughters. A definite ingrowth of radon daughters occurs before reaching the second filter where they are collected. A surface-barrier detector located within 5mm of the second filter is used to measure the alpha spectrum of the radon daughters. The concentration of the radon isotopes can be calculated by entering these daughter count rates into a suitable computer program (128). This method eliminates the possible error that can occur in the gross counting method which assumes that all daughter counts come from radon-222 only.

Normally, radon-219 will be a small fraction of the radon-222 concentration. This is because of the low activity of the uranium-235 series relative to the uranium-238 series (approximately 5% for natural abundances) and also, the short half-life of radon-219 (4 s). Only those atoms generated on the surface of solids will be able to diffuse into the surrounding air before they decay. Under certain conditions, the long-lived parents of radon-219, namely protactinium-231 and actinium-227, may be concentrated at the surface of tailings particles. This will give rise to a higher ratio of radon-219 to radon-222 than would be the case where the radon parents are distributed evenly throughout each particle. Such abnormalities have been observed in the Nordic tailings from the Elliot Lake area (211).

11.2 INTERFERENCES

No radioactive elements.

11.3 APPARATUS

- Air filters: Cellulose acetate membrane filters
- Air pump: Constant-rate motor-operated
- Flowmeter: Calibrated using a wet-test meter
- Surface barrier detector: 450 mm^2
- Bias power supply
- Multichannel analyzer.

11.4 REAGENT

- Helium supply.

11.5 PROCEDURES

1. The apparatus is assembled as in the schematic shown in Figure 7. Air is pulled through the filter at a flowrate of approximately 12 L/min. An air filter, #1, is located at the sample inlet to prevent dust from being deposited on filter #2 and to remove airborne radon daughters. The flow is monitored with a flowmeter. A surface barrier detector is positioned within 5 mm of filter #2.
2. The sampling time will depend on the relative activity levels of the radon isotopes. Since Pb-211, the longest-lived Rn-219 daughter, has a half-life of 36.1 min, and the long-lived daughter of Rn-220, Pb-212, has a half-life of 10.6 h, a sample time of 1 h should be adequate.
3. At the end of the sample period, flush the chamber containing the surface barrier detector with helium.
4. Count the activity trapped on the filter for 10 min, starting 2 min after the end of sampling. A spectrum similar to that in Figure 8 should be obtained on the multichannel analyzer. The resolution will depend on the completeness of the helium flush and the degree of penetration of the daughters into the filter's surface.
5. The count rate is determined over each of the four energy regions:
   a) 5.20–6.16 MeV (Bi-212, Po-218);
   b) 6.16–6.75 MeV (Bi-211);
   c) 6.75–8.10 MeV (Po-214, Po-215);
   d) 8.10–9.50 MeV (Po-212).
6. Recount the sample for 15 min, starting 15 min after the end of sampling.

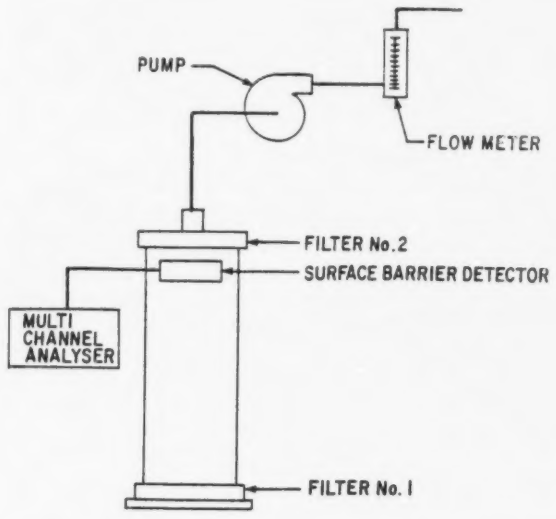

Fig. 7 – Schematic of two-filter apparatus for measuring radon isotopes in the field.

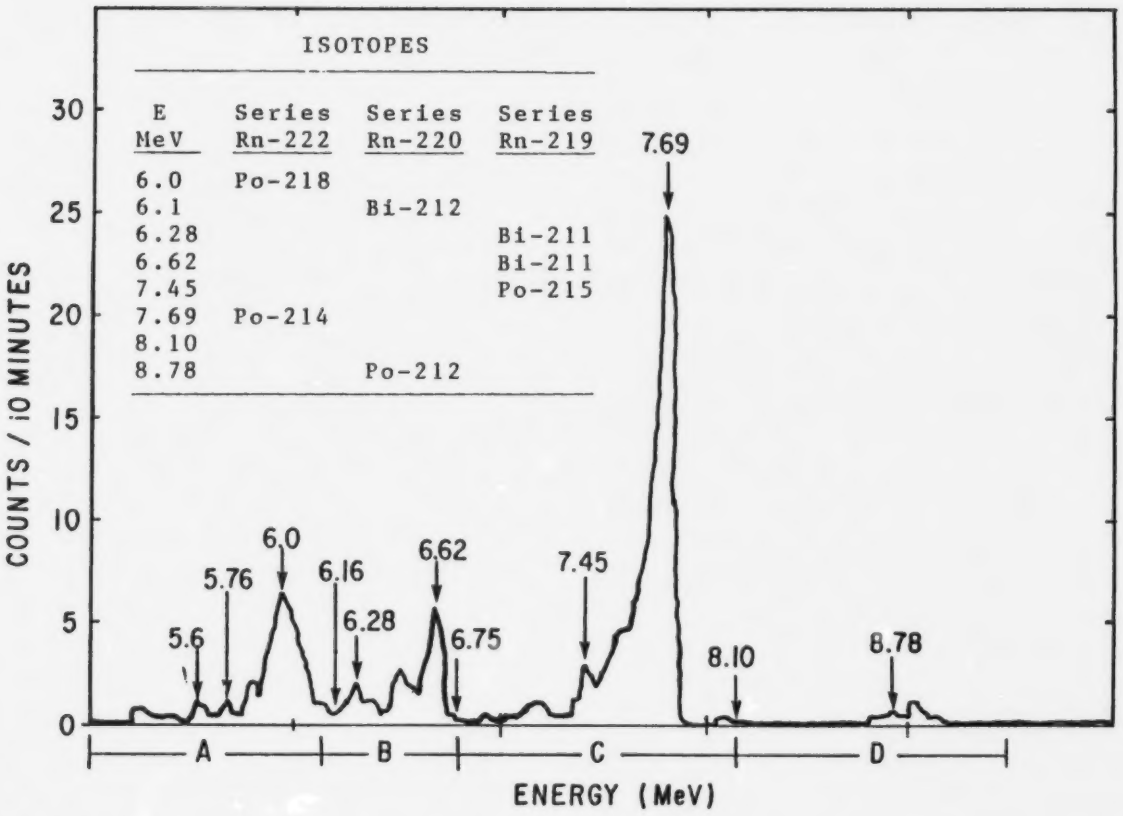

Fig. 8 – Alpha spectrum obtained for radon, using the two-filter apparatus. Presence of Rn-222, Rn-220 and Rn-219 is indicated. The various energies are identified (124).

7. Perform a final count beginning approximately 300 min after the end of sampling.
8. These three measurements allow the calculation of activities of Pb-211 and Bi-211 (daughters of Rn-219), Po-218, Pb-214 and Bi-214 (daughters of Rn-222) and Po-212 (daughter of Rn-220).

11.6 CALCULATIONS

1. Counts from each region are used to calculate the activities of Rn-222, Rn-220 and Rn-219 according to the equations described by Kerr (212) and Perdue et al. (128).
2. To know the airborne concentrations of radon daughters in the sampled air, filter #1 must be removed.
3. In summary, the experimental information required to make these calculations are:
   - start time of atmospheric sampling;
   - sample rate;
   - efficiency of detector;
   - counts for regions a, b, c and d (see step 5 above) for the three sample periods;
   - starting and stopping time of each count interval.
4. The program accounts for the energy overlap between Bi-212 and Po-218 in region a, but the counts for Bi-212 can be subtracted as they are approximately equal to 0.56 times the counts in region d. A correction is made for the overlap of Bi-211 from region b into region a.

12. DETERMINATION OF URANIUM

Two very sensitive methods for the determination of uranium are described here. The first is the fluorometric method which requires a fluorometer (151–160). The second is the bromo-PADAP spectrophotometric method which requires a spectrophotometer (148,159).

12.1 FLUOROMETRIC METHOD

12.1.1 Principle

Uranium fused with sodium fluoride produces a brilliant yellow green fluorescence when exposed to ultraviolet light. This technique is specific for uranium when the excitation wavelength is 365 nm. The intensity of the fluorescence is proportional to the amount of uranium present.

12.1.2 Interferences

Many cations interfere by quenching the uranium fluorescence intensity. These include Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Sn, W, Pt, Au, Hg, Pb, La, Th, Ce, Pr and Nd. Some cations interfere by enhancing the uranium fluorescence even though by themselves they do not fluoresce in fluoride phosphors. These include Ca, Mg, V, Be, Mo, Nb and Sb. These interferences can be eliminated either by dilution or by extracting uranyl nitrate into ethyl acetate or methyl isobutyl ketone, as detailed by Donaldson (159).

12.1.3 Apparatus

- Fluorometer
- Fusion dishes: Platinum or platinum–rhodium, the size and shape to be determined by the requirements of the fluorometer
- Trays for fusion dishes: Aluminum block with holes to fit fusion dishes
- Fusion burner: Commercially available and capable of a 1000°C temperature
- Infrared heat lamp
- Micropipette: 100-µL with disposable tips
- Macropipette: 5–10 mL with disposable tips
- Extraction bottles: 40-mL polyethylene centrifuge tube with screw cap
- Vortex mixer: Variable speed.

12.1.4 Reagents

- Standard uranium solution (100 µg/mL): Dissolve 117.9 mg of pure U_3O_8 in 20 mL of 16 N HNO_3 with heating. Cool and dilute to 1 L with deionized water
- Aluminum nitrate solution (2 g/mL): Dissolve 2 kg of $Al(NO_3)_3 \cdot 9H_2O$ in deionized water and dilute to 1 L
- Flux pellets (0.6 g): 98% sodium fluoride and 2% lithium fluoride
- Ethyl acetate: Reagent grade
- Hydrofluoric acid (50%): Reagent grade
- Nitric acid (16 N): Reagent grade
- Perchloric acid (70%): Reagent grade.

12.1.5 Preparation

12.1.5.1 Water

Samples with uranium concentrations below the detection limit (50 ppb) must be concentrated. For a 10:1 concentration, transfer 100 mL to a 150-mL Teflon TFE beaker, add 5 mL each of 16 N HNO_3 and 50% HF, and evaporate to dryness. Cool, add 5 mL 20% HNO_3 to dissolve residue and transfer quantitatively to a 10-mL volumetric flask. Rinse beaker with 2–3 mL of deionized water, add to flask and make up to volume.

12.1.5.2 Tailings, soils, sediments, biological ashes and air filters

Digest an aliquot (0.1–0.5 g) of the solid sample or a 47-mm air filter in a 150-mL covered Teflon TFE beaker with 5 mL each of 16 N HNO_3, 50% HF and 70% $HClO_4$ at low heat until clear. Remove cover and evaporate almost to dryness. Cool. Add 5 mL of 25% HNO_3 and boil for few minutes. Cool, transfer to a 25-mL volumetric flask and make up to volume with deionized water.

WARNING: Perchloric acid is a very powerful oxidizing acid and should be handled with extreme care. All evaporation must be done in a perchloric acid fumehood.
(For details see Section 2.5.6 Procedure F.)

12.1.5.3 General

For direct determination, begin at step 4. For extraction method, begin at step 1.

1. Place 10 mL of the $Al(NO_3)_3$ solution in a 40-mL screw-cap centrifuge tube. Add an aliquot (up to 1.0 mL) of sample solution and 10 mL of ethyl acetate.
2. Securely cap the tube and mix thoroughly for one minute using a vortex mixer.
3. Let stand to allow layers to separate.
4. Place a flux pellet in each of the platinum fusion dishes.
5. Using a micropipette, transfer two 100-µL aliquots of the sample solution or ethyl acetate extract onto each of two flux pellets and dry under an infrared heat lamp.
6. Prepare duplicate samples, blanks and standards.
7. Place the fusion dishes on the fusion burner and fuse for 30 s at 400°C and 2.5 min at 1000°C. Cool for 15 min. (This timing is important.)

8. Measure fluorescence following the instructions supplied by the fluorometer manufacturer.

   Note: Segregate platinum dishes for high, medium and low levels of uranium. After each use, wash each dish with hot water, fuse with 0.5 g of potassium pyrosulfate, cool and dissolve flux in hot water. Store the dishes in 1 N HNO_3 and rinse with deionized water before use.

12.1.6 Calculations

The quantity of uranium, U, in the sample pellets is expressed in nanograms per 100 µL and is calculated as follows:

$$U = \frac{R_s - R_b}{R_u - R_b} \times Q_u$$

where:

R_b = mean reading of duplicate blanks

R_s = mean reading of duplicate samples

R_u = mean reading of duplicate uranium standards

Q_u = quantity of uranium standard in pellet, ng.

The uranium concentration in the original samples can be calculated when the appropriate dilution, concentration and extraction factors are used.

12.1.7 Precision

For the direct measurement, the precision is ±15%. The precision for the extraction method is poorer because of the additional manipulation.

12.2 BROMO-PADAP SPECTROPHOTOMETRIC METHOD

12.2.1 Principle

Uranium and bromo-PADAP, (2-(5-bromo-2-pyridylazo)-5-diethylaminophenol) react to form a coloured complex, which can be determined by spectrophotometry. The complex is developed in an ethanol–water mixture at pH 7.6, and in the presence of a mixed complexing solution containing 1,2-cyclohexylenedinitrilotetraacetic acid (CyDTA), sulphosalicylate and fluoride. The wavelength of maximum absorbance is at 578 nm. Uranium extracted into tri-n-octylphosphine oxide (TOPO) in cyclohexane can be determined directly in the extract. In this case, the colour complex gives maximum absorbance at a wavelength of 574 nm and at pH 8.35.

12.2.2 Interferences

Many cations interfere by complexing with bromo-PADAP. However, most of these are eliminated in the presence of the mixed complexing solution of CyDTA, sulphosalicylate and fluoride, which functions as a masking agent. Cations which interfere significantly (Fe, Ce, Th, V, Zr) are eliminated by the TOPO/cyclohexane extraction. Anions such as sulfate and chloride should preferably be absent as they may enhance the extraction of some of the interfering cations. Phosphate has no effect on uranium extraction up to the 500-mg level. Therefore, this method is particularly suited to high-phosphate samples such as phosphate ores.

12.2.3 Apparatus

- Spectrophotometer: With 10-mm and 50-mm absorption cells
- Volumetric test tubes: Calibrated at 25 mL and 50 mL
- Vortex mixer
- Disposable test tubes: 25 mm × 160 mm.

12.2.4 Reagents

- Standard uranium solution (100 µg/mL): See Fluorometric Method (Section 12.1.4)
- Bromo-PADAP (0.05%): Dissolve 250 mg of bromo-PADAP in 500 mL of ethanol
- Complexing solution: Add 25 g of CyDTA, 5 g of NaF and 65 g of sulfosalicyclic acid to 800 mL of deionized water. Adjust pH to 7.85 with 10 N NaOH and dilute to 1 L
- Dilute complexing solution: Dilute one part of the complexing solution with an equal volume of deionized water, and adjust the pH to 8.35 with 10 N NaOH
- Buffer solution (pH 7.85): Dissolve 149 g of triethanolamine in 800 mL of water, adjust pH to 7.85 with perchloric acid and allow to stand overnight. Readjust if necessary and dilute to 1 L
- Buffer solution (pH 8.35): Same as above, but adjust pH to 8.35
- TOPO solution (0.1 M): Dissolve 19.3 g of tri-n-octylphosphine oxide in 500 mL cyclohexane
- Sodium fluoride solution (2% w/v): Dissolve 2.0 g of NaF in 100 mL of deionized water.
- Ascorbic acid (5% w/v): dissolve 5.0 g of ascorbic acid in 100 mL of deionized water.

12.2.5 Procedures

12.2.5.1 Sample preparation

See Section 12.1.5.

12.2.5.2 Direct measurement

1. Pipette an aliquot of water sample (up to 6–7 mL) into a volumetric test tube.

   Note: Determine on a separate aliquot the volume of 1 N NaOH required for neutralization.

2. Add 2.0 mL of complexing agent. Mix.
3. Add 2.0 mL of pH 7.85 buffer solution. Mix.
4. Add the volume of 1 N NaOH determined in step 1 above. Mix.

5. Add 10.0 mL of ethanol and 2.0 mL of bromo-PADAP solution. Mix.
6. Dilute to 25 mL volume with deionized water. Mix.

   Note: pH of solution should be 7.6.
7. Allow to stand for 1 h, measure the absorbance at 578 nm with a spectrophotometer after zeroing the instrument with a reagent blank.
8. Prepare a standard curve by carrying the following standards through the entire procedure, 0.0, 1.0 μg, 5.0 μg, 10.0 μg, 20.0 μg, 40.0 μg, 60.0 μg and 100 μg of uranium.

12.2.5.3 Extraction

1. Pipette an aliquot (up to 25 mL) of the sample into a 25-mm × 160-mm test tube, add 5 mL of 2% NaF solution and 2 mL of 5% ascorbic solution and mix.
2. Add 5.0 mL of TOPO solution and mix vigorously for 1 min using a vortex mixer. Allow the phases to separate.
3. Pipette 2.0 mL of the TOPO extract into a dry volumetric test tube.
4. Add 1.0 mL of dilute complexing solution. Mix.
5. Add 4.0 mL of bromo-PADAP solution. Mix.
6. Add 1.0 mL of pH 8.35 buffer solution. Mix.
7. After 15 min, add 16.0 mL of ethanol, dilute to 25 mL with deionized water and mix.
8. Measure the colour at 576 nm after zeroing the instrument with a reagent blank.
9. Prepare a standard curve by carrying a series of standards through the complete extraction.

12.2.6 Calculation

Determine the uranium concentration in the sample from the equation:

$$\mu g\ U \text{ per mL} = \frac{\mu g\ U \text{ from standard curve}}{\text{mL sample aliquot}}.$$

The uranium concentration in the original sample can be calculated when the appropriate dilution, concentration and extraction factors are used.

12.2.7 Precision

The expected relative precision is 10%.

REFERENCES

1. Krieger, H.L. and Whittaker, E.L., Report EPA-600/4-80-032. USEPA, Cincinnati, OH., p.10 (1980).
2. Goldin, A.S., Anal. Chem., 33, 406 (1961).
3. Smithson, G.L., CANMET Report 78-22, EMR Canada, Ottawa, Ont., (1978).
4. Kenzie, A.B., Baxter, M.S., McKinley, I.G., Swan, D.S. and Jack, W. Radioanal. Chem., 48, 29 (1979).
5. Michel, J. and Moore, W., Health Phys., 38, 663 (1980).
6. Percival, D.R. and Martin, D.B., Anal. Chem., 46, 1742 (1974).
7. Sill, C.W., Health Phys., 33, 393 (1977).
8. John, F.B., Hahn, P.B., Thome, D.G. and Bretthauer, E.W., Report EMSL-LV-0539-17, USEPA, Las Vegas, NV., (1979).
9. Harley, J.H. ed., EML Procedure Manual HASL-300, Env. Meas. Lab., USDOE, New York, NY., 1972, Procedure E-Ra-03.
10. Kobal, I., Shahin, M., Kristan, J. and Senegavik, M., Health Phys., 27, 381 (1974).
11. Lucas, H.F., Rev. Sci. Instrum., 28, 680 (1957).
12. Mastinu, G.G., Health Phys., 28, 97 (1975).
13. Rushing, D.R., Garcia, W.J. and Clark, D.A., in "Radiological Health and Safety in Mining and Milling of Nuclear Materials," IAEA, Vienna, Austria, 187 (1964).
14. Kobal, I. and Kristan, J., Radiochem. Radioanal. Letters, 10, 291 (1972).
15. Higgins, F.B.Jr., Grune, W.N., Smith, B.M. and Terrill, J.G.Jr., J. Am. Water Works Assoc., 53, 63 (1961).
16. Hursh, J.B., J. Am. Water Works Assoc., 46, 43 (1954).
17. Darrall, K.G., Richardson, P.J. and Tyler, J.F.C., Analyst, 98, 610 (1973).
18. Zarov, P.N., Radiokhimiya, 2, 630 (1960).
19. Sebesta, F. and Obdrzalek, M., J. Radioanal. Chem., 59, 119 (1980).
20. Sedlacek, J., Sebesta, F. and Benes, P., J. Radioanal. Chem., 59, 45 (1980).
21. Michel, J., Moore, W.S. and King, P.T., Anal. Chem., 53, 1885 (1981).
22. Moore, W.S. and Reid, D.F., J. Geophys. Res., 78, 8880 (1973).
23. Moore, W.S., Deep-Sea Res., 23, 647 (1976).
24. Bland, C.J., in "Natural Radiation Environment III", USDOE Symp. Ser., 51, 633 (1980).
25. Ku, T.L., Huh, C.A. and Chen, P.S., Earth Planet, Sci. Lett., 49, 293 (1980).
26. Chung, Y., ibid., 49, 319 (1980).
27. Wicke, A., and Porstendoerfer, J., J. Radioanal. Chem., 56, 105 (1980).
28. Powers, R.P., Turnage, N.E. and Kanipe, L.G., in "Natural Radiation Environment III," USDOE Symp. Ser., 51, 640 (1980).
29. Trahey, N.M., Voeks, A.M. and Soriano, M.D., Report NBL-303, USDOE, Argonne, IL, p. 131 (1982).
30. Ibid., p. 116 and p. 117 (1982).
31. Schery, S.D., Anal. Chem., 52, 1957 (1980).
32. McCurdy, D.E. and Mellor, R.A., Anal. Chem., 53, 2212 (1981).
33. Lowe, D.M., Kennett, T.J., Prestwich, W.V. and Tsai, J.S., J. Radioanal. Chem., 78, 359 (1983).
34. Martin, M.J. and Blichert-Toft, P.H., "Nuclear Data Table," Academic Press, New York, NY, pp. 125–143 (1970).
35. Sill, C.S., Health Phys., 17, 89 (1969).
36. Zimmerman, J.B. and Armstrong, V.C., CANMET Report 76-11, EMR Canada, Ottawa, Ont. (1976).
37. Keisch, B. and Levine, A.S., Anal. Chem., 38, 1969 (1966).
38. Lim, T.P. and Davé, N.K., CIM Bulletin, 74, 97 (1981).
39. Sedlet, J., in "Treatise on Analytical Chemistry," I.M. Kolthoff and P.H. Elving, Ed., Part II, Vol. 4, Interscience, New York, NY, pp. 219–366 (1966).
40. Dean, J.R. and Chiu, N., Nucl. Instrum. Methods, 233, 253 (1984).
41. Sill, C.W., private communication.
42. Noyce, J.R., NBS Technical Note #1137, National Bureau of Standards, Washington, DC, (1980).
43. Baratta, E.J. and Feldman, M.H., Topical Report WIN-123, U.S. Atomic Energy Commission (1961).
44. Humphrey, H.W., Adkins, E.L. and Templin, G.G., Report NLCO-1084, U.S. Atomic Energy Commission (1975).
45. Iyer, R.H., Jain, H.C., Ramaniah, M.V. and Rao, C.L., Radiochem. Acta, 5, 56 (1966).
46. Johnson, J.O., Water Supply Paper 1696-G, U.S. Geological Survey, Washington, DC, (1971).

47. Kahlos, H. and Asikainen, M., Report SFL-A-19, Institute of Radiation Physics, Helsinki Finland (1973).

48. Knauss, K.G., Ku, P.L. and Moore, W.S., Earth Planet. Sci. Lett., 39, 235 (1978).

49. Koide, M. and Bruland, K.W., Anal. Chem. Acta, 75, 1 (1975).

50. Krieger, H.L., Report EPA-600/4-75-008 (Revised), USEPA, Cincinnati, OH. (1976).

51. Petrow, H.G. and Allen, R.J., Anal. Chem., 33, 1303 (1961).

52. Petrow, H.G., Cover, A., Scheissle, W. and Parsons, E., Anal. Chem., 36, 1600 (1964).

53. Sakanoue, M.T., Nomura, T., Imai, T. and Vzuyama, H., Proceedings of Symposium on Hydrogeochemistry and Biogeochemistry, Tokyo, Japan, Vol. 1, p. 293 (1973).

54. Sekine, T., Koike, Y. and Sakairi, M., J. Nucl. Sci. Tech., 4, 308 (1966).

55. Smith, K.A. and Mercer, G.R., J. Radioanal. Chem., 5, 303 (1970).

56. Kaufman, A., Trier, R.M., Broecker, W.S. and Feely, H.W., J. Geophys. Res., 78, 8827 (1973).

57. Kuchta, D.R., Rundo, J. and Holtzman, R.B., Proceedings of Symposium on Biological and Environmental Effects of Low-Level Radiation, Chicago, IL., Vol. II, p. 183 (1976).

58. Tomza, I., Proceedings of the International Conference on Low-Radioactivity Measurements and Applications, Czechoslovakia, p. 387 (1977).

59. Chiu, N. and Dean, J.R., Internal Procedure Manual, Monenco Analytical Laboratories, Calgary, Canada (1983).

60. Sill, C.W. and Williams, R.L., Anal. Chem., 53, 412 (1981).

61. Krebs, C.A. and Whipple, G.H., Report No. UR-501, University of Rochester, Atomic Energy Project (1957).

62. MacKenzie, A.B. and Scott, R.D., Analyst (London), 104 and 1151 (1979).

63. Helmkamp, R.W., Bale, W.F. and Hrynyszyn, V., Int. J. Applied Radiat. Isotopes, 30, 237 (1979).

64. Blanchard, R.L., Anal. Chem., 38, 189 (1966).

65. Gotchy, R.L. and Schiager, K.J., Health Phys., 17, 199 (1969).

66. Cohen, N. and Kneip, T.J., Health Phys., 17, 125 (1969).

67. Erbacher, O. and Philipp, K., Z. Physik, 51, 318 (1928).

68. Robbins, M.C., Report LA-1904, Los Alamos Scientific Lab., Univ. of California (1955).

69. Gloebel, B., Muth, H. and Oberhausen, E., Strahlentherapie, 131, 218 (1966).

70. Black, S.C., Health Phys., 7, 87 (1961).

71. Erbacher, O. and Philipp, K., Z. Phys. Chem., A150, 214 (1930).

72. Petrow, H.G. and Cover, A., Anal. Chem., 37, 1659 (1965).

73. Sill, C.W. and Willis, C.P., Anal. Chem., 37, 1661 (1965).

74. Aronson, A.L. and Hammond, P.B., Nucleonics, 22, 90 (1964).

75. Talvitie, N.A. and Garcia, W.J., Anal. Chem., 37, 851 (1965).

76. Harrison, A.D.R., Lindsey, A.J. and Phillip, R., Anal. Chim. Acta, 13, 459 (1955).

77. Milland, H.T., Anal. Chem., 35, 1017 (1963).

78. Gorsuch, P.T., Analyst, 84, 135 (1959).

79. Jaworolski, Z., Nukleonika, 8, 333 (1963).

80. Sandell, E.B., "Colorimetric Determinations of Traces of Metals", Interscience, New York, NY, (1959).

81. Bambach, K. and Burkey, R.E., Ind. Eng. Chem. Anal. Ed., 14, 904 (1942).

82. Korkisch, J. and Feik, F., Anal. Chem., 36, 1793 (1964).

83. Tshimori, P., Bull. Chem. Soc. Japan, 28, 432 (1955).

84. Dedek, W., Z. Anal. Chem., 173, 399 (1960).

85. Bhattacharyys, D.K., Separation Science, 9, 257 (1970).

86. Frieson, W.J. and Jons, J.W., Anal. Chem., 23, 1447 (1951).

87. Dicky, E.E., J. Chem. Educ., 30, 525 (1953).

88. Levi, M.C. and Danon, J., J. Chromatogr., 3, 584 (1960).

89. Sato, P.R., Norris, W.P. and Strain, H.H., Anal. Chem., 27, 521 (1955).

90. Conte, P. and Muxart, R., J. Chromatogr., 3, 96 (1960).

91. Smithson, G.L., CANMET Report 78-22, EMR Canada, Ottawa, Ont., p. 55 (1978).

92. Pehl, R.H., Phys. Today, 30, 11 and 50 (1977).

93. Sill, C.W., Anal. Chem., 49, 618 (1977).

94. Sill, C.W., Puphal, K.W. and Hindman, F.D., Anal. Chem., 46, 1725 (1974).

95. Hyde, E.K., "The Radiochemistry of Thorium", NAS-NS-3004 (1960).

96. Wrenn, M.E., Singh, N.P., Ibrahim, S.A. and Cohen, N., Anal. Chem., 50, 1712 (1978).

97. Petrow, H.G., Sohn, B. and Allen, R.J., Anal. Chem., 33, 1301 (1961).

98. Durham, R.W. and Joshi, H.R., J. Radioanal. Chem., 52, 181 (1979).

99. Sill, C.W., Anal. Chem., 36, 675 (1964).

100. de Villiers, A.H. and Windish, J.P., Brit. J. Ind. Med., 21, 94 (1969).

101. Rock, R.L., "Sampling Mine Atmospheres for Potential Alpha Energy Due to the Presence of Radon-220 (Thoron) Daughters", MESA Information Report 1015 (1974).

102. Busigin, A., Van der Voorem, A.W. and Phillips, C.R., "Attached and Unattached Radon Daughters; Measurements and Measurement Techniques in Uranium Mines and in the Laboratory", Atomic Energy Control Board, Canada, Ottawa, Ont., December (1978).

103. Busigin, A.W., Van der Voorem, H.H., Lin, P. and Phillips, C. R., Mineral Sci. Eng., 11, 193 (1979).

104. Janka, K. and Lehtimaki, M., Rev. Sci. Instrum., 53, 523 (1982).

105. McLaughlin, J.P. and Nolan, P.J., Proc. R. Ir. Acad., 68, 55 (1969).

106. Dalu, G.A. and Dalu, G., Atti. Conv. Ass. Geofis. Ital., 19, 791 (1969).

107. Dalu, G. and Dalu, G.A., J. Aerosol Sci., 2, 247 (1971).

108. Morse, R.H., "Radon Counters in Uranium Exploration", International Atomic Energy Agency, Vienna, Austria (1976).

109. Czarnecki, R.F. and Pacer, J.C., USDOE Report GJBX-13(83), Grand Junction, CO, (1983).

110. Fleischer, R.L., Hart, H.R. and Mogro-Camero, A., Nucl. Instrum. Methods, 173, 169 (1980).

111. Fremlin, J.H. and Abu Jarad, F., Nucl. Instrum. Methods, 173, 197 (1980).

112. Fremlin, J.H. and Abu Jarad, F., Nucl. Instrum. Methods, 173, 201 (1980).

113. Nakahara, H., Kudo, H., Alba, F. and Murakami, Y., Nucl. Instrum. Methods, 171, 171 (1983).

114. Cohen, B.L. and Cohen, E.S., Health Phys., 45, 501 (1983).

115. Maki, Y. and Tanaka, F., J. Radioanal. Chem., 79, 141 (1983).

116. Prichard, H.M., Health Phys., 45, 493 (1983).

117. Murakami, Y., Horiuchi, K., J. Radioanal. Chem., 52, 275 (1979).

118. Shearer, S.D. and Sill, C.W., Health Phys., 17, 77 (1969).

119. Sill, C.W., Health Phys, 16, 371 (1969).

120. George, A.C. and Breslin, A.J., "Measurements of Environmental Radon with Integrating Instruments", in "Methods for Measuring Radiation in and around Uranium Mills". E.D. Harwood, ed., Atomic Industrial Forum, Inc., Washington, DC, (1977).

121. Nyberg, P.C., and Bernhardt, D.E., Health Phys., 45, 539 (1983).

122. Thomas, J.W., EML Procedures Manual HASL-327, Env. Meas. Lab., USDOE, New York, NY, (1977).

123. McVey, J.R., Franklin, J.C. and Shaw, D.M., Min. Congress J., 6, 49 (1977).

124. Wrenn, M.E., Spitz, H. and Cohen, N., IEEE Trans. Nucl. Sci., 22, 645 (1975).

125. Scheibel, H.G., Porstendorfer, J. and Wicke, A., Nucl. Instrum. Methods, 165, 345 (1979).

126. Schery, S.D., Gaeddert, D.H. and Wilkening, M.H., Rev. Sci. Instrum., 51, 338 (1980).

127. Nazaroff, W.W., Rev. Sci. Instrum., 54, 1277 (1983).

128. Perdue, P.T., Legett, R.W. and Haywood, F.F., in "Natural Radiation Environment III", DOE Symp. Ser., 51, 347 (1980).

129. Rodden, C.J. ed., "Analytical Chemistry of the Manhattan Project", McGraw-Hill, New York, NY, 1950.

130. Rodden, C.J., Anal. Chem., 25, 1598 (1953).

131. Rodden, C.J. and Tregoning, J.J., "Manual of Analytical Methods for the Determination of Uranium and Thorium in Their Ores", U.S. Government Printing Office, Washington, DC, 1955.

132. Grimaldi, F.S., May, I. and Fletcher, H.H., U.S. Geol. Survey Circ #199 (1952).

133. Grimaldi, F.S., May, I. Fletcher, M.H. and Titcomb, I., U.S. Geol. Survey Bull #1006 (1954).

134. Palei, P.N., "Analytical Chemistry of Uranium", translated by N. Kaner, Ann Arbor-Humphrey Science Publishers, Ann Arbor, MI, 1970.

135. Savvin, S.B. Talanta, 8, 673 (1961).

136. Ibid., 11, 1 (1964).

137. Ibid., 11, 7 (1964).

138. Kadam, B.V., Maiti, B. and Sathe, R.M., Analyst, 106, 724 (1981).

139. Isaeva, A.A., Golovanov, V.I. and Presnyakova, O.E., Radiokhimiya, 19, 94 (1977); Chem Abstr., 87, 11209x (1977).

140. Ohnishi, K., Hori, Y. and Tomari, Y., Buneski Kagaku, 26, 74 (1977); Chem Abstr., 86, 176952b (1977).

141. Chung, K.T., Fen Hsi Hua Hsueh, 7, 106 (1979); Chem. Abstr., 92, 64187y (1980).

142. Keil, R., Z. Anal. Chem., 297, 384 (1979); Chem. Abstr., 91, 203808W (1979).

143. Reinhardt, K.H. and Mueller, H.J., Z. Anal. Chem., 292, 359 (1978); Chem. Abstr., 90, 28790q (1979).

144. Geary, W.J., Nickless, G. and Pllard, F.H., Anal. Chim. Acta, 26, 575 (1962).

145. Sommer, W., Ivanov, V.M. and Novotna, H., Talanta, 14, 329 (1967).

146. Florence, T.M. and Farrar, Y.J., Anal. Chem., 35, 1613 (1963).

147. Pakalns, P., Anal. Chim. Acta, 120, 289 (1980).

148. Johnson, D.A. and Florence, T.M., Anal. Chim. Acta, 53, 73 (1971).

149. Lyle, S.J. and Tamizi, M., Anal. Chim. Acta, 121, 341 (1980).

150. Pakalns, P., Mikrochim Acta, 1, 339 (1980); Chem. Abstr., 94, 52552s (1981).

151. Krieger, H.L. and Whittaker, E.L., "Prescribed Procedures for Measurement of Radioactivity in Drinking Water," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinatti, OH, 1980, Method 908.1.

152. Bodnar, L.Z. and Percival, D.R., "Analytical Chemistry Branch Procedures Manual," U.S. Department of Energy, Radiological and Environmental Sciences Laboratory, Idaho Falls, ID, 1982, Method U-1.

153. Hues, A.D., Henicksman, A.L., Ashley, W.H. and Romero, D., "The Fluorometric Determination of Uranium in Natural Water," Los Alamos Scientific Laboratory Informal Report LA-6683-MS, 1977.

154. Owens, J.W., "Fluorometric Determination of Uranium in Environmental Materials," Los Alamos Scientific Laboratory Informal Report LA-6338-MS, 1976.

155. Centanni, F.A., Rosa, S.M. and DeSesa, M.A., Anal. Chem., 28, 1651 (1956).

156. Price, G.R., Ferretti, R.J. and Schwartz, S.S., Anal. Chem., 25, 322 (1953).

157. "1983 Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, PA, 1983, Volume 11.01, Method D2907-75.

158. Harley, J.H., ed., EML Procedures Manual HASL-300, Env. Meas. Lab., USDOE, New York, NY, 1972, Method E-U-01.

159. Donaldson, E.M., "Methods for the Analysis of Ores, Rocks and Related Materials," 2nd Ed., Energy, Mines and Resources Canada, Ottawa, Canada, 1982, p. 251.

160. McElhaney, R.J., Caylor, J.D., Cole, S.H., Futrell, T.L. and Giles, V.M., Report Y-2111, National Technical Information Services, Springfield, VA, 1978.

161. Stephens, F.B., Hangen, G.R. and Richardson, J.H., Report UCID-17549, National Technical Information Service, Springfield, VA, (1977).

162. Campen, W. and Baechmann, K., Mikrochim. Acta, 2, 159 (1979); Chem. Abstr., 92, 134971a (1980).

163. Hinton, E.R., Jr. and White, L.E., Anal. Lett., 14, 947 (1981).

164. Perry, D.L., Klainer, S.M., Bowman, H.R., Milanovich, F.R., Hirschfeld, T. and Miller, S., Anal. Chem., 53, 1048 (1981).

165. White, L.E., Report Y-2205, National Technical Information Service, Springfield, VA, (1980).

166. Johnston, M.V. and Wright, J.C., Anal. Chem., 53, 1050 (1981).

167. Zook, A.C. and Pietri, C.E. in Anal. Chem. Nucl. Technol., Proc. Conf. Anal. Chem. Energy Technol., W.S. Lyon, ed., Ann Arbor Science, Ann Arbor, MI, pp. 41–7 (1982).

168. Zook, A.C. and Collins, L.H., U.S. NBS Special Publ., 582, 147 (1980).

169. Bian, Y.S., Huanjing Baohu, 6, 28 and 37 (1981).

170. Lyon, W.S., Radiochem. Radioanal. Lett., 22, 357 (1975).

171. Lyon, W.S., Radiochem. Radioanal. Lett., 23, 1 (1975).

172. Lyon, W.S., Radiochem. Radioanal. Lett., 29, 223 (1977).

173. Brits, R.J.N. and Smith, M.C.B., Anal. Chem., 49, 67 (1977).

174. Holzbecker, J. and Ryan, D.E., Anal. Chim. Acta, 119, 405 (1980).

175. Kuleff, I. and Kostadinov, K.N., J. Radioanal. Chem., 46, 365 (1978).

176. Hirose, A. and Ishii, D., J. Radioanal. Chem., 46, 211 (1978).

177. Ward, F.N. and Price, V., J. Geochem. Explor., 13, 97 (1980).

178. Hathaway, L.R. and James, G.W., Anal. Chem., 47, 2035 (1975).

179. Carovajal, G.S., Mahan, K.I. and Leyden, D.E., Anal. Chim. Acta, 135. 205 (1982).

180. Burba, P., Gleitsmann, B. and Lieser, K.H., Z. Anal. Chem., 289, 28 (1978); Chem. Abstr., 88, 126113z (1978).

181. Vane, R.A., Stewart, W.D. and Barker, M., Adv. X-ray Anal., 23, 81 (1980).

182. Amos, M.D. and Willis, J.B., Spectrochim. Acta, 22, 1325 (1966).

183. Martin, M.J., Analyst, 96, 843 (1971).

184. Mavrodineanu, R. and Bioteux, H., "Flame Spectroscopy", Wiley, New York, NY, p. 429, (1965).

185. Alder, J.F. and Das, B.C., Analyst, 102, 564 (1977).

186. Alder, J.F. and Das, B.C., At. Absorpt. Newsl., 17, 63 (1978).

187. Scott, R.H., Strasheim, A. and Kokot, M.L., Anal. Chim. Acta, 82, 67 (1976).

188. Homi, C.S. and Manabe, R.M., Proceedings of the 23rd Conference on Analytical Chemistry in Energy Technology held in Gatlinburg, TN, p. 335 (1979).

189. Sill, C.W. and Willis, C.P., Anal. Chem., 49, 302 (1977).

190. Sill, C.W., U.S. NBS Special Publication #422, 463 (1976).

191. Harley, J.H., ed., EML Procedures Manual HASL-300, Env. Meas. Lab., US DOE, New York, NY, (1972), Procedure E-Sr-01.

192. Smithson, G.L., CANMET Report 78-22, EMR Canada, Ottawa, Ont., p. 53 (1978).

193. Smith, G.F., Anal. Chim. Acta., 8, 397 (1953).

194. Chemical Safety Data Sheet SD-11, Manufacturing Chemists Association of the U.S., Washington, DC, (1965).

195. Schumacher, J.C., ed., "Perchlorates", ACS Monograph No. 146, American Chemical Society, Washington, DC, (1960).

196. Bland, C.J., Int. J. Applied Radiation and Isotopes, 35, 279 (1984).

197. Bodnar, L.Z. and Percival, D.R., "Analytical Chemistry Branch Procedures Manual," U.S. Department of Energy Radiological and Environmental Licences Laboratory, Idaho Falls, ID, 1982, Method GA/B-2.

198. Krieger, H.L. and Whittaker, E.L., "Prescribed Procedures for Measurement of Radioactivity in Drinking Water," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1980, Method 900.0.

199. "1983 Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, PA, 1983, Volume 11.01, Methods D1943-81 and D1890-81.

200. "Standard Methods for the Examination of Water and Wastewater," 15th Ed., American Public Health Association, Washington, DC, 1980, Method 703.

201. Harley, J.H., ed., EML Procedures Manual HASL-300, Env. Meas. Lab., US DOE, New York, NY, 1972, Procedure E-00-05.

202. Wayman, N.A., Glissmeyer, J.A., Silker, W.B. and Endres, G.W.R., "Methods for Assessing Background Levels of Radiation and Radioactive Materials in the Environment Around Uranium Mills," U.S. Nuclear Regulatory Commission, Battelle Pacific Northwest Laboratory, Richland, WA, 1980, Section 6.0.

203. Sill, C.W. and Olson, D.G., Anal. Chem., 42, 1596 (1970).

204. Steger, H.F. and Smith, C.W., CANMET Report MRP/MSL 83-149 (J), EMR Canada, Ottawa, Ont., (1983).

205. Krieger, H.L. and Whittaker, E.L., Report EPA-600/4-80-80-032, USEPA, Cincinnati, OH, p. 47 (1980).

206. Ibid., p. 49 (1980).

207. Bazzano, E. and Gersini, G., Anal. Chim. Acta, 38, 457 (1967).

208. Westland, A.D. and Kantipuly, C.J., Talanta, 30, 751 (1983).

209. Anon., PG Report 685 (W), U.K. At. Energy Auth. Rep., Lancashire, England (1965).

210. Thomas, J.W. and Le Clare, P.C., Health Phys., 18, 113 (1970).

211. Lim, T.P. and Davé, N.K., CANMET Elliot Lake Lab., Elliot Lake, Ont., personnal communication.

212. Kerr, G.D., Trans. Am. Nucl. Soc., 17, 542 (1973).

APPENDIX A

Estimation and Reporting of Procedural Uncertainties (Precision) in Radiochemical Determinations

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Estimation and Reporting of Procedural Uncertainties (Precision) in Radiochemical Determinations

It is incumbent upon radiochemists carrying out isotopic activity determinations to estimate uncertainties in their reported measurements. Failure to do so invites misinterpretation or misuse of the data. Every analytical report should contain an unambiguous statement of the estimated magnitude of uncertainty associated with each report result. Furthermore, the calibration standard reference materials (SRM) and methodology employed should be referenced. This is particularly important in the age of multi-laboratory measurement programs and widely accessed databases.

Various publications have dealt with the problem of ambiguity in reporting of uncertainties associated with measured values (A.1–A.4). Sill outlines a protocol relevant to radiochemical measurements to be employed by the Analytical Chemistry Branch of a U.S. Energy R & D Laboratory (A.1). Miedema has prepared an assessment of reporting results from the chemical/radiochemical laboratory at Eldorado Resources Ltd. and suggested a reporting protocol (A.4). Some features of these were adopted in the following proposed convention for reporting uncertainties.

1. SI units should be employed, e.g., Bq/g for specific activity. (One picocurie is equivalent to exactly 0.037 becquerels by definition.)
2. Each result should be accompanied by a plus/minus estimate of the in-laboratory precision of the measurement. The precision estimate should be an 'entire procedure' value as determined in the laboratory making the measurement. The significance level of the estimate should be indicated (1σ, 2σ...); in keeping with past practice, and for uniformity, the one sigma level is recommended. Calibration SRM activities and half-lives involved in the activity calculation should be treated as absolute constants in estimating this precision.
3. Values below the 'detection limit' should be reported as calculated with their corresponding uncertainties.
4. The identity and total uncertainty of the SRM used for the activity measurements should be cited as a potential source of bias of the calculated value with respect to the absolute activity. Currently accepted values of half-lives, or isotopic specific activities, should be used and cited.
5. Example:

Sample	Ra 226 found	Bq/g
84-3401	0.02 ± 0.04	(1σ)
84-3402	14.80 ± 0.44	(1σ)
84-3403	-0.01 ± 0.04	(1σ)

Note:

The uncertainties shown reflect the estimated precision of the measurements. The reported values are relative to NBS SRM 4959-193 having a total estimated uncertainty of ±1.26% in radium-226 mass. The radium-226 specific activity 3.659×10^4 Bq/μg and $t_{1/2}$ = 1599 years were used for the activity conversion and SRM decay correction. Radium-226 was determined by alpha spectrometry following its isolation from the matrix (Radioanalytical Methods Manual, National Uranium Tailings Program, Chiu and Dean, eds., Energy, Mines and Resources Canada, (1985).

The procedures in this manual indicate formulae for calculating the uncertainty (σ_{cs}) in a determined activity value due to propagation of the uncertainties in counting measurements entering into the activity calculation. The sections on precision also indicate that there are other contributions to the total method precision (σ_T) such as pipetting errors, counting geometry, representative sampling, etc. The combined effects of these are likely to exhibit normal (Gaussian error) behaviour for the method as applied within a given laboratory, characterized by an effective standard deviation (σ_p). Assuming that σ_p is activity-independent, the relation

$$\sigma_T^2 = \sigma_{cs}^2 + \sigma_p^2$$

provides a means of estimating the effective value of σ_p from replicate determination of the isotope activity in a homogeneous reference material. The counting error should be held constant (and ideally small compared to the total uncertainty) for the estimation. The value of σ_T (and hence σ_p) can then be estimated from the standard error (s_n) of n replicate, independent measurements as

$$\hat{\sigma}_T = (t_{0.05,n-1}/1.96) \times s_n$$

where:

$$s_n = \left[\sum_i^n (A_i - \bar{A})/(n-1) \right]^{0.5}$$

where:

A_i = determined activity,

$\bar{A}$ = mean of n measurements,

$t_{.05,n-1}$ = student's t at the 5% significance level for n − 1 degrees of freedom,

1.96 = error interval in σ units that contain 95% of all values for a rigorously Gaussian distribution.

The factor ($t_{0.05,n-1}/1.96$) allows for the uncertainty in the approximation $\bar{A} = \bar{A}_x$ when n is small.

Ideally, through an effective development and quality control program, σ_p's will be estimated by the laboratory from replicate measurements on a number of different homogeneous materials related to the sample types to be measured and realistic operative values will be established. These may then be used with calculated values of σ_{cs} to estimate total laboratory precisions.

Total laboratory uncertainty may also be estimated by propagation of statistical errors of the parameters entering the calculation (A. 5), provided these can be independently estimated, and that all significantly variable parameters are included.

Expression of laboratory uncertainties as "one-sigma" implies that the Gaussian probability distribution applies to the repeatability of the measurement within the laboratory. That is, the laboratory expects, on reasonable statistical grounds, that the reported value would differ from the mean value in a large number of measurements by more than 1.96σ with only a 5% probability, or more than 2.58σ with only a 1% probability. In order that this implication be realistic at least to the 5% significance level (95% confidence level), it is suggested that standard errors of components determined from small numbers of measurements be multiplied by the appropriate factor, as shown in Table A.1, to estimate effective sigma values used in propagation formulae.

Table A.1. Values of student's t at the 5% significance level divided by 1.96

n − 1	$t_{0.05,n-1}/1.96$
1	6.48
2	2.19
3	1.62
4	1.42
5	1.31
6	1.25
7	1.20
8	1.18
9	1.15
10	1.14
15	1.09
20	1.07

REFERENCES

A.1. Sill, C.W. "Reporting of analytical results"; In Requirements for an Effective National Ionizing Radiation Measurements Program, NBS Special Publication 603; pp. A15–A18; Washington, National Bureau of Standards; 1981.

A.2. Eisenhart, C. "Expression of the uncertainties of final results"; In Precision Measurements and Calibration: Statistical Concepts and Procedures, Special Publication 300, Volume 1; Washington, National Bureau of Standards; 1969. (Reprint from Science 160: 1201–1204; 1968.)

A.3. Ku, H.H. "Expressions of imprecision, systematic error and uncertainty associated with a reported value"; op. cit. (Reprint from Measurements and Data, July–August: pp. 72-77; 1968.)

A.4. Miedema, M.C. "The reporting of results from the analytical laboratory"; Report AR84-2; Eldorado Resources Ltd.; 1984.

A.5. Ku, H.H. "Statistical concepts in metrology"; In Precision Measurements and Calibration: Statistical Concepts and Procedures, Special Publication 300, Volume 1; Washington, National Bureau of Standards; 1969. (Reprint from Handbook of Industrial Metrology, American Society of Tool and Manufacturing Engineers; pp. 20–50; New York, Prentice-Hall, 1967.)